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ELEMENTS OF CHEMISTRY.

ELEMENTS OF CHEMISTRY:

THEORETICAL AND PRACTICAL.

BY
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HONI SOIT QUI MAL Y PENSE
SANCTE ET SAPIENTER

PART III.

ORGANIC CHEMISTRY.

LONDON:
JOHN W. PARKER AND SON, WEST STRAND.
1857.

LONDON:
AND EDWARDS, PRINTERS, CHANDOS STREET,
COVENT GARDEN.

PREFACE.

In the work of which the present volume forms the third and concluding portion, it has been the aim of the author to give the leading facts and doctrines of chemical science, in as concise a form as possible, without sacrificing clearness and accuracy to brevity. But in order that the reader may be enabled to refer to original sources when further information is needed, references have been given to the papers from which the more important details have been obtained, particularly to the recent memoirs on organic chemistry.

It will be observed that in the arrangement of the present volume, free use has been made of the system of classification in homologous series, which was employed with such admirable results by the late highly gifted M. Gerhardt, whose early removal from the scene of his indefatigable and successful labours the scientific community have had so recently to deplore.

The general method of classification adopted by that eminent chemist, in his *Traité de Chimie Organique*, excellent as it is in many respects for the advanced cultivator of the science, is not, however, well adapted to the plan of a didactic work like the present; and it was judged preferable, after a preliminary sketch of the methods of investigation and classification employed, to commence the detailed description of the products of organic chemistry with that of a few of the best known and most familiar compounds derived from the vegetable kingdom, although their composition is less simple than that of many other organic substances; for this reason sugar, starch, and vegetable fibre were made the starting point; and from them the transition was easy to the processes of fermentation, and the comprehensive group of alcohols, and their derivatives the ethers and allied compounds.

In treating these various classes of compounds, the author preferred to examine successively the different members of each homologous group, before passing to the consideration of the derivatives from the typical or leading member of each group. For instance, in the case of ordinary alcohol, instead of describing ether, aldehyd, and acetic acid in succession, the different varieties of alcohol, such as wood spirit, fousel oil, &c., are first described; then aldehyd and its homologues; after them the series of the vinic acids, and then that of the ethers. By thus presenting the different members of the same homologous series in succession to the student (see p. 33), he is enabled to trace more readily their similarities and their differences, and to note the general method adopted in their preparation, than if his attention were distracted by passing to other bodies of totally different character and properties. This plan conduces to brevity as well as to clearness, and facilitates the description of the various series from a more general point of view, than would be readily practicable, if the arrangement followed by most writers since the appearance of

Liebig's classical work on organic chemistry were followed.

The homologous and the collateral series may be compared to a number of ladders placed side by side against a house. The terms of a homologous series succeed each other like the rounds of a ladder, whilst the terms of the derived and collateral series are like those of a second or a third ladder placed by the side of the first. It is safer and easier to ascend or to descend the steps of each ladder in succession, than to step across from one ladder to the other.

In the nomenclature of the alcohols and their derivatives, the principle introduced in the case of the hydrocarbons by Berzelius, and more fully carried out by Gerhardt, has been followed, with the view of avoiding the confusion which would have been introduced into this portion of the subject, had the names which are frequently employed to designate them been retained; for example:—

$$\underbrace{\overbrace{(C_8H_8)_2}^{\text{Butylene.}}}_{\text{Tetrylene.}} \quad \underbrace{\overbrace{(C_8H_9)_2}^{\text{Butyl.}}}_{\text{Tetryl.}} \quad \underbrace{\overbrace{(C_8H_7O_2)}^{\text{Butyryl.}}}_{\text{Butyryl.}} \quad \underbrace{\overbrace{(C_8H_9O,\ HO)}^{\text{Butylic Alcohol.}}}_{\text{Tetrylic Alcohol.}} \quad \underbrace{\overbrace{(HO,\ C_8H_7O_3)}^{\text{Butyric Acid.}}}_{\text{Butyric Acid.}},$$

the lower series of terms being those adopted in the present work; and in order to escape the confusion between *butyl* the radicle of the alcohol, and *butyryl* the radicle of butyric acid, the Greek term *tetryl* has been substituted for that of *butyl;* the series derived from the alcohol being thus distinguished from that derived from the acid. Names formed upon this principle, it is true, are often less euphonious than those which they are designed to displace; but it is better to sacrifice euphony than precision, and the new terms have the advantage of distinctly recalling the proportions of carbon which are present in the respective compounds indicated.

It is necessary to remark that certain acids, particularly the carbonic, the oxalic, the sulphuric, and the sulphurous, are treated in the first and second portions of the work as though they were monobasic; whilst in the third part they are viewed as dibasic. At the same time it was stated (pp. 574, 645, 1162) that there are many circumstances which render it probable that the latter hypothesis is the more correct one. It appeared to be convenient to retain in the elementary portion of the work, the older view which regards these acids as monobasic, and which has been hitherto assumed in all treatises published previous to that of Gerhardt. The necessity for theoretical explanations at an early point in the work was thus obviated, and the simplicity in the formulæ usually adopted was preserved. In the complicated phenomena of organic chemistry, however, the results of experiment are more readily interpreted by assuming that these acids are dibasic.

In the closing chapter of the work, a careful review of Kopp's researches upon atomic volumes and the boiling point of organic liquids, is given: and it is hoped that the comparison of the results of Andrews upon the heat of combination with those obtained by Favre and Silbermann upon the same subject, will be found of value and of interest to others besides the student.

In conclusion, the author desires to express his sincere thanks to his friend Mr. C. Tomlinson, who has with untiring kindness revised the proof sheets of the entire work, and has made several valuable suggestions during its progress. To his friend and colleague, Professor Bloxam, he is also indebted for the revision of the proof sheets of a large portion of the third volume, and to his patience and accuracy the author desires to acknowledge his obligation.

It may be mentioned that the equivalent of antimony has recently been redetermined by Schneider; and according to his experiments, which have been confirmed by H. Rose, the equivalent number of this metal should be reduced from 129·0 to 120·3.

The difficulty of ensuring complete accuracy in the printing of complicated chemical formulæ can be known only to those who have had to see a work of this kind through the press. Since these sheets have been printed, several minute errors have been discovered, which are included in a table of errata at the end of the work. The student will do well to make the corrections indicated previous to reading the book.

King's College, London,
February, 1857.

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PART III.

ORGANIC CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

Analysis of Organic Compounds;—Principles of Classification;—Metamorphoses of Organic Compounds.

(897) ORGANIC CHEMISTRY, in its primary signification, is that division of the science which treats of the chemistry of organized beings, and of the products of their chemical actions upon matter in its various forms.

It is important *in limine* to draw a clear distinction between *organic compounds* and *organized bodies.*

Organic compounds, like those derived from the mineral kingdom, possess a definite composition, and in many cases exhibit a perfectly definite crystalline structure. Bodies, such as sugar, urea, taurin, quinia, and acetic acid, belong to this class; such substances are often spoken of as the *proximate principles* of animals and vegetables: many of them may be obtained from inorganic bodies by synthesis.

On the other hand, organized bodies, such as muscular tissue, nervous structure, cellulose, and ligneous fibre, never exhibit any tendency to crystalline structure, but show a rounded, vesicular, or fibrous configuration; and are so connected with each other as to form parts of a system, each of which is incomplete if severed from the remainder. Bodies such as these cannot be prepared synthetically: they are the result of the action of living bodies upon inanimate matter; a living body having the power of assimilating fresh particles, and of arranging them in the special form which characterizes the class to which the individual organism belongs.

The study of the chemical changes that occur during these transformations, constitutes *physiological chemistry,* the most difficult branch of the science. Its difficulty depends, however, not upon the obscurity which enshrouds the nature of life itself; for the essential nature of every description of force, and of the mysterious tie which exists between matter and force, has baffled the penetration of the profoundest philosophers, and belongs to an order of truths to which the human intellect probably may not be permitted in this sphere of its existence to attain.

The difficulty in the study of the chemical changes that occur in the living animal or plant depends rather upon the extreme delicacy of the arrangements by which these metamorphoses are effected; and upon the complicated nature of those arrangements, which are liable to injury from a multiplicity of causes that have hitherto eluded scrutiny. Other difficulties arise from the facility with which important changes are effected in the organism itself without being appreciable to human sense, save in their results, although they may even proceed so far as to occasion death. The ligature of a large artery or the section of a nerve effects an alteration which can be at once appreciated; but when an animal is poisoned by a fraction of a grain of aconitine or by a few drops of hydrocyanic acid, nothing indicates to the anatomist, to the microscopic observer, or to the chemist, the mode in which these bodies operate in suddenly cutting short the life of the animal. The organization still appears to be perfect, yet the living laboratory no longer continues to perform its wonted operations, and the inanimate mass speedily falls under the dominion of ordinary chemical laws. In the living body, ordinary chemical affinities are suspended, and compounds are produced, which, when released from the influences under which they originated, quickly undergo fresh changes, which are manifested by the occurrence of putrefaction and decay, to which both animal and vegetable bodies are liable when they no longer form parts of the living frame. Occasional instances of instability, somewhat analogous to those exhibited by organized bodies, are seen in some of the compounds of inorganic chemistry; but this perpetual tendency to change is one of the distinguishing and essential characteristics of living bodies. When the plant or the animal is performing its functions in a healthy manner, these changes succeed each other in a defined and regular order; but if this sequence be modified, even in a slight degree, disease generally ensues, and when the alteration reaches a certain amount or degree, death is the speedy and inevitable consequence.

In the present work the attention of the reader will be only incidentally directed to the physiological portion of the subject, the main object being to exhibit the mutual relations which the different chemical compounds bear to each other, and to trace the laws of their formation. Even with these limitations the subject of organic chemistry is one of great extent and complexity.

(898) *Organic products* are composed of a small number of elements: yet such products present properties as much opposed to each other as it is possible to imagine; some constituting the daily food of man, others acting as direct and violent poisons: yet these very different bodies rarely consist of more than four elements, viz., carbon, hydrogen, nitrogen, and oxygen; a few contain minute proportions of sulphur and phosphorus, with certain earthy and saline matters.

The presence of carbon is so uniform in organic bodies, that generally one of the most convenient means of ascertaining if an unknown body be of organic origin, is to heat a fragment of it in a narrow test tube; the carbon is thus separated, and the substance becomes charred and blackened, except in a few cases where the material may be wholly volatilized without undergoing decomposition. Several of the essential oils, such as those of turpentine, elemi, juniper, and attar of roses, consist of carbon and hydrogen only: the same may be said of naphthalin, benzole, and the illuminating constituents of coal gas: but the larger number of organic bodies contain carbon, hydrogen, and oxygen; this occurs, for example, in the case of sugar, acetic acid, alcohol, the fixed oils, and the greater part of the proximate principles of vegetables. Nitrogen is superadded to these elements in many instances, though such compounds are of less frequent occurrence, except in highly organized portions of the plant or animal, such as the seed, or the muscular and other animal tissues; albumen, fibrin, indigo, quinia, and the vegetable alkalies generally, contain nitrogen as an essential component. The presence of nitrogen may in most cases be ascertained readily by heating a small fragment of the substance in a tube with hydrate of potash, when a distinct odour of ammonia is perceived.

The organs by which these various compounds are produced always contain small quantities of alkaline and earthy salts, among which the compounds of potassium, sodium, calcium, and magnesium, in combination with chlorine, and with sulphuric, phosphoric, and silicic acids, are the most frequent: in rarer cases oxides of iron and manganese are met with, and in still rarer instances, fluorine, iodine, and bromine. The presence of certain of these saline bodies appears to be as essential a condition to the chemical activity of the growing plant or animal as that of carbon, of hydrogen, or of oxygen. Besides these natural components of organic products, the chemist often artificially introduces other elements for the purpose of dissecting, as it were, these compounds, and of ascertaining the probable rational composition of the body under experiment. With this view he either produces new compounds which contain sulphur, phosphorus, chlorine, nitrous acid, or sulphuric acid; or he obtains others in which arsenic, antimony, zinc, and a variety of metallic compounds, are substituted for a portion of the hydrogen of the original substance.

(899) *Organic and Inorganic Compounds.*—Many distinguished philosophers have attempted to define the difference between organic and inorganic chemistry. Thus, Laurent has termed organic chemistry 'the chemistry of carbon,' and Liebig has defined it as 'the chemistry of compound radicles.' Few persons, however, would be disposed with Laurent, to consider carbonic acid as an organic compound, and many chemists regard sulphurous acid, which is undoubtedly a compound inorganic substance, as the radicle of a somewhat numerous series of bodies of inorganic origin.

There is, in fact, no definite line of demarcation between inorganic and organic products. Amongst the productions of organized nature, acids, alkalies, salts, and other bodies are met with, similar in chemical functions to those derived from inanimate nature; and all organic compounds are subject to precisely the same chemical laws as those which regulate the combinations and decompositions of bodies confessedly inorganic; but the composition of the former being generally much more complicated than that of the latter, the balance of affinity in organic bodies is disturbed by slighter causes; and there are consequently an unnumbered variety of products generated by slight modifications of the various forces to which organic substances are subjected.

Still, for convenience sake, it is advisable to classify chemical compounds in some measure according to their origin; since those derived from the inorganic world, from the greater simplicity of their composition, afford to the student the most favourable instances for examining the fundamental laws of chemical combination, before he proceeds to the investigation of the more complicated products obtained from operations of the living vegetable or animal.

The number of organic compounds known to chemists is very great, and the list is perpetually undergoing increase; it therefore cannot excite surprise, if amongst them numerous instances of isomerism, metamerism, and polymerism (413) should occur.

The formation of ***isomerides, metamerides***, and ***polymerides***, as bodies which possess the same percentage composition may be termed, can only be accounted for by supposing that differences of chemical arrangement occur in these different cases. In some instances a rational explanation of the cause of difference may be given. A familiar example is afforded in the case of two metamerides, acetate of methyl, and formic ether. These two bodies are liquids, which each contain $C_6H_6O_4$, they have nearly the same boiling point and specific gravity, and yield vapours of the same density; but there can be no doubt that they are differently constituted. The acetate of methyl is prepared by the action of acetic acid upon wood spirit, and acetic acid may be extracted from it by means of an alcoholic solution of potash, whilst wood spirit is liberated; formic ether is the result of an action of formic acid upon ordinary alcohol, and when treated with potash in the same way as the acetate of methyl, betrays its origin by yielding formic acid and alcohol. The two bodies may therefore be represented as constituted very differently, thus:—

$$\overbrace{C_2H_3O,\ C_4H_3O_3}^{\text{Acetate of Methyl.}} = (C_6H_6O_4)\text{; and,}$$

$$\overbrace{C_4H_5O,\ C_2HO_3}^{\text{Formic Ether.}} = (C_6H_6O_4).$$

In other cases, such for example as the ordinary sugar of fruits ($C_{12}H_{12}O_{12}$), no reasonable hypothesis of its composition has been offered; yet we know of the existence of several bodies isomeric with it, such as hydrated lactic and acetic acids, for which a rational formula (282) has been suggested.

Even in substances of comparatively simple composition, the difficulty of framing a conclusive theory of their molecular arrangement is very great, as may be seen by inspecting the following table, which represents a few of the views which have been taken respecting the nature of hydrated acetic acid:—

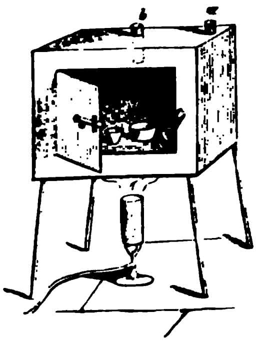
$C_4H_4O_4$. . . .	Hydrated Acetic Acid.	(Empirical formula.)
HO, (C_4H_3), O_3	Hydrate of teroxide of Acetyl.	(Liebig.)
$\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2$	. . . .	(Gerhardt.)
HO, (C_2H_3), C_2O_3.	Methyloxalic Acid . . .	(Kolbe.)
HO, $C_2(C_2H_3)O_3$.	Methylformic Acid . . .	(Wurtz.) (Gerhardt.)

It must however be borne in mind, that conjectures such as these as to the internal arrangement of organic bodies do but represent probabilities, which may sometimes be so great as almost to amount to certainty. The rational formulæ which embody these views, should therefore be regarded simply in the light of *memoria technica;* means by which facts may be riveted upon the memory, and by which analogies that otherwise would escape the notice of the observer may be traced; and, above all, as instruments by which that precision may be given to our ideas, which is so essential to the reception and advancement of solid philosophical knowledge.

On the Analysis of Organic Compounds.

(900) *Proximate Analysis.*—In the analysis of organic compounds, two problems are presented to the chemist for solution:—the object of the first, is to separate the proximate components of the vegetable or animal product from each other; whilst the object of the second, is to determine the elementary composition of the proximate principles thus isolated. The separation of wheat flour into starch, sugar, gluten, ligneous fibre, and oily matter, affords an instance of *proximate* analysis; but the determination of the proportions in which the carbon, hydrogen, and oxygen are united in the component starch, sugar, or fibre, furnishes an illustration of what is meant by *ultimate* organic analysis.

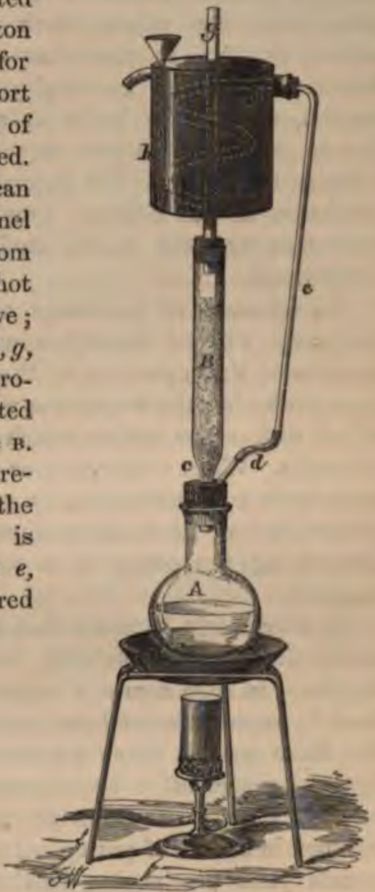
Fig. 325.



The proximate analysis of an organic compound is often a matter of great difficulty. The first process generally consists in the complete desiccation of a given weight of the substance under examination, by exposing it to a temperature of from 212° to 250° in a *water oven* or box of sheet copper, made double, as shown in Fig. 325; *a* being an aperture for the introduction of oil or of water into the interval between the external and internal plates, the temperature being regulated by a thermometer introduced at *b*. The loss of weight which the substance under examination experiences during the drying can be accurately ascertained when needed. The dried material is then pulverized, and subjected to the action of several solvents in succession, such as ether, alcohol, and water.

A convenient apparatus for the digestion of the substances for analysis in these menstrua, is shown in fig. 326:—A is a glass flask filled with the liquid to be employed as the solvent; this can be kept in steady ebullition by the lamp beneath. B, is a tube of glass or of tin-plate, in the contracted portion of which is a plug of cotton wool, *c*; in this tube the substance for analysis is to be placed; *d*, is a short lateral tube to which the tube, *e*, of glass or of flexible metal is attached. M is a tin-plate condenser, which can be filled with water; *h*, is a funnel for conveying cold water to the bottom of this refrigerator, whilst the hot water flows off at the spout above; through the axis of M passes a tube, *g*, open at both ends; the lower projecting extremity of this tube is fitted by a cork to the top of the tube B. *f* is a worm tube, the upper extremity of which passes through the side of the refrigerator, and is adapted by a cork to the tube *e*, whilst its lower extremity is soldered to the tube *g*, into which its contents flow after they have been condensed in their passage through the refrigerator. It is obvious that by this arrangement a perpetual distillation of the liquid in the flask A, may be readily maintained; the vapour which passes through the tube *e*, becomes condensed in the spiral tube *f*, and percolates, in the liquid form, through the material contained in B, carrying the soluble matters into the flask A, where they gradually accumulate. If the employment of metal be in any case objectionable, glass vessels may be used, but they are more fragile and more costly than those made of metal.

Fig. 326.



Ether is particularly valuable as a solvent for fatty substances, and for caoutchouc and camphor; alcohol, for the solution of many crystallizable organic principles, such as the vegetable alkalies; whilst water dissolves sugar, gum, starch, and other bodies, which are nearly insoluble in alcohol and in ether. In some cases benzole, in others chloroform, is a valuable solvent, and may be substituted for ether, which they most resemble in their solvent action. In particular cases dilute acids, and in others dilute alkalies may be employed, but they must be used with caution, as they are liable to act not merely as solvents, but also to produce important chemical changes upon the compounds submitted to them. No general rule can be laid down for the extraction of the different proximate principles; each class of substances requiring special modifications, which experience alone can indicate.

In all cases of proximate analysis, the employment of the microscope will be found invaluable as a means of watching the progress of the separation of the various principles, and of ascertaining whether the substances which the chemist has isolated are mixed with other bodies which may resemble them in chemical habitudes. When a substance or a deposit assumes the crystalline state, such an examination, by revealing the similarity or difference in form of its component particles, is often more valuable for ascertaining the purity of a substance than ordinary chemical reagents.

It frequently happens that two or more substances, of different degrees of solubility in the same menstruum, occur together: in such a case, if crystallizable, they may often be separated by repeated crystallizations, care being taken always to separate those crystals which are first deposited from those which are formed subsequently: by successive recrystallizations of the first portions from each crop, the least soluble compound may be obtained in a state of purity. In other cases, if the different compounds yield precipitates with the same reagent, but differ in the degree of their affinity for it, a separation may be effected by adding a quantity of the precipitant insufficient to throw down, for example, more than one-half of the amount of substances that may be present. The salts of silver or of lead may thus be added to mixtures of various organic acids, particularly to such as, like the fatty acids, greatly resemble each other in properties. The precipitate is then suspended in water, and decomposed by means of sulphuretted hydrogen, or a dilute mineral acid, in order to separate the metal, and liberate the acid, which is again submitted to a similar incomplete precipitation; and this process is repeated until the fusing point becomes constant, or till some other guarantee of the purity of the body is obtained.

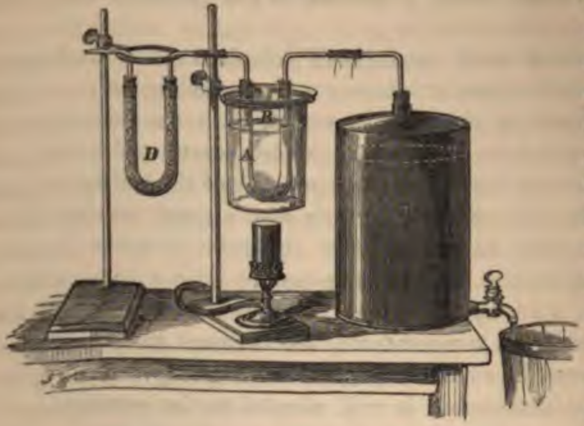
In the rectification of mixtures of volatile liquids, analogous principles are acted upon; in these cases the boiling point is the guide. The liquid is placed in a retort, into the tubulure of which a thermometer is fitted, and the temperature is raised till the liquid boils. So long as the temperature of the boiling liquid continues to rise, the substance which distils must consist of a mixture; but as soon as the point of ebullition becomes nearly stationary, the distillate may be supposed to have a composition nearly uniform; and by rectifying again those portions which distil at the same fixed temperatures, the different components of a mixed liquid may be obtained in a state of purity. This process of *fractional* distillation is well adapted to the separation of liquids, the boiling points of which differ considerably from each other; but it does not answer when they are within 20° or 30° of each other.

Liebig has applied a modification of this method to the separation of certain volatile acids from each other; and it may be employed generally in such cases with advantage. This process consists in saturating a portion of the acid liquid with potash or soda, and then proceeding with the distillation; the more volatile acid passes over with the distillate. Suppose that it be desired to effect the separation of butyric from valerianic acid:—a certain amount of potash is added, and if this be more than sufficient to saturate the valerianic acid, the distillate will consist of butyric acid only, while the residue will be a mixture of valerate and butyrate of potash. If, on the other hand, the valerianic acid be more than sufficient to saturate the potash, the residue in the retort will consist of pure valerate of potash, and the distillate will be a mixture of butyric and valerianic acids, which may be separated by a repetition of the same process.

(901) *Ultimate Analysis.*—Before proceeding to the ultimate analysis of a body, it is first carefully dried either in the *water oven*, or by means of an apparatus similar to that shown in Fig. 327, in which A represents a bent glass tube, in which the substance to be dried is placed; B, a glass or metallic vessel, con-

taining water, or some saline solution; C, an aspirator, by which a current of atmospheric air can be maintained through the apparatus; and D, a bent tube filled with fragments of pumice-stone, soaked in oil of vitriol, for drying the air as it enters. The desiccation must be continued as long as the tube A ceases to lose weight. If the desiccation be effected in the water oven, the capsule or crucible must be allowed to cool under a shade, over a dish of oil of vitriol, and must be kept covered whilst being weighed, in order to prevent the absorption of moisture.

FIG. 327.



(902) *Determination of the Mineral Components.*—If any mineral substances be present in the compound under examination, the amount of these must be ascertained by the incineration of a weighed quantity of the material. This operation, simple as it may appear, is one, the exact performance of which is attended with considerable difficulty, which arises from the partial volatilization of the alkaline chlorides at a red heat, and the reduction of the sulphates to the form of sulphides. The incineration should, therefore, always be performed at a low temperature, which need not exceed a barely visible red, but must be prolonged for many hours if the mass for incineration be considerable. M. Caillat finds it advantageous in a large number of cases, previous to incineration, to treat the substance with dilute nitric acid, by which means almost the entire saline ingredients may be extracted in the soluble form; on incinerating the insoluble portion, scarcely anything is left except silica and a small quantity of peroxide of iron. The quantity of saline matters thus obtained always exceeds that furnished by the former method; since in the digestion with nitric acid the loss occasioned by reduction of the sulphate of lime, and the partial expulsion of sulphur from the sulphide of

calcium so formed, is avoided; the proportion of sulphuric acid obtained is therefore always higher than when incineration is employed.

(903) Since the four elements, carbon, hydrogen, oxygen, and nitrogen, constitute the bulk of most organic substances, the operation of organic analysis resolves itself mainly into the accurate quantitative determination of these elements. We are indebted to Gay Lussac and Thénard for the fundamental principle that regulates our operations in this respect. The process proposed by them has subsequently been modified and improved by many chemists, especially by Berzelius, Prout, and Liebig, and it was by the last named eminent philosopher that the method now in general use was contrived.

The object of this enquiry being to determine the relative proportion in which each of the ultimate elements exists, it becomes necessary to the success of any analytical process that these elements should be procured either separately in a state of purity, or in the form of definite compounds that can easily be collected; and it has been found most convenient, by supplying the substance to be analysed with a sufficient quantity of oxygen, to convert the carbon into carbonic acid, which may be absorbed by potash and weighed, and the hydrogen into water; the water, also, by passing it over a substance that has a powerful attraction for it, such as chloride of calcium or sulphuric acid, may be collected and weighed; whilst the nitrogen is collected and measured in the form of gas, over mercury.

In certain cases where nitrogen is present, the substance to be analysed may be mixed with hydrate of soda or of potash, and heated; all the nitrogen is thus converted into ammonia, in which form, like carbonic acid, and water, it admits of being weighed. It is easy to find by calculation the weight of the carbon, the hydrogen, and the nitrogen respectively contained in the carbonic acid, the water, and the ammonia collected. When the proportion of saline matter has been determined by incineration of a portion of the mass, the quantity of oxygen which the substance contains may be known by deducting the united weight of the carbon, the hydrogen, the nitrogen, and the salts from the total weight of the body analysed; the deficiency (supposing sulphur and phosphorus not to have been present) is reckoned as oxygen.

Scrupulous attention to the purity of the matter submitted to analysis is of course of primary importance, a very slight admixture with other compounds being sufficient to vitiate the conclusions deducible from the experiments. Having by suitable means ascertained the purity of the substance for analysis, the next care is to ensure its complete desiccation. Solids should be dried in the water oven in the manner already directed. Volatile liquids that are unchanged by distillation should be allowed to stand for two or three days upon fragments of fused chloride of calcium; the liquid should then be decanted and distilled in a small retort. In other cases, as in the examination of fats or fixed oils, it may be more convenient to dry the material in a watch-glass placed in an ordinary water-bath, or the hot-water oven previously described. The further progress of the analysis will vary according to the form and composition of the substance to be examined.

We shall describe the methods of analysing—

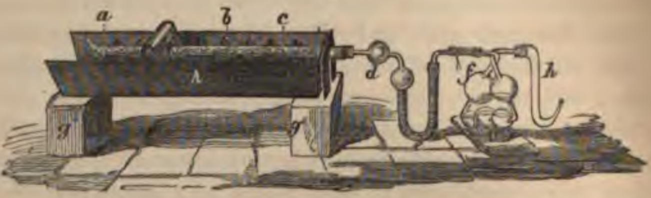
1. A *solid,* which does not contain nitrogen.
2. A *liquid,* which does not contain nitrogen.
3. A substance, which does contain nitrogen.

1. *Analysis of a solid not containing nitrogen.*

(904) The combustible which answers best in these experiments is charcoal; it is very manageable, but the dust occasioned by it is troublesome. Spirits of wine or pyroxylic spirit are cleaner, but their expense is a great objection. Dr. Beale and Dr. Hofman have contrived furnaces in which gas is made use of as a fuel, but the apparatus is liable to get out of order. (*Quart. Journ. Chem. Soc.,* 1853, 209.)

The best form of furnace to be used with charcoal is represented at A, fig. 328: it is made of stout sheet-iron bent into the form of a trough, open at one end; the plate which closes the other end is perforated with an aperture three-quarters of an inch in diameter, to allow the passage of the combustion tube; the furnace is about twenty inches long, five inches wide at top, two inches and three-quarters at bottom, and three inches high. Transverse slits are made along the floor at intervals of two inches for the admission of air, and between each of these slits are riveted vertical stiff

Fig. 328.



pieces of sheet-iron, one inch high, terminating in a concave edge above, for the support of the combustion tube. During the operation, the apparatus may rest on bricks, *g, g*.

The tube in which the mixture is burned, ***the combustion*** or ***retort tube***, (*a, b, c*,) should be of difficultly fusible glass free from lead, about fifteen inches long and half an inch in diameter: the hard Bohemian glass answers the purpose perfectly. The tube may on certain occasions be drawn out into a fine but strong tail bent upwards at an obtuse angle, and the mouth should be smoothed by making it red hot in the flame of the blowpipe, so that a cork need not be torn in adjusting it.

The water is collected in a bent tube, *e*, filled with chloride of calcium. At *d* is a small bulb, in which the greater part of the water is condensed; it may be emptied from time to time. The chloride of calcium with which the bent portion is filled must not be fused, but should be prepared merely by evaporating the solution of the chloride to dryness by a strong sand heat. A porous mass is thus obtained, which does not crystallize by absorbing moisture, as the fused variety does, to the destruction of the tube that contains it. The cork through which passes the bent tube by which it is connected with the potash bulbs, *f*, should be trimmed close to the large tube and covered neatly with melted sealing-wax; and, lastly, air should be drawn through the apparatus by the mouth to ascertain that no obstruction exists. Pumice-stone moistened with concentrated sulphuric acid may be advantageously substituted for chloride of calcium in the drying tube.

The connexion between this tube and the retort, *a, b, c*, is effected by means of a sound elastic cork, which is made to close the mouth of the tube accurately; it is pierced with a round file, and fitted firmly upon the fine tube proceeding from the bulb *d* of the drying tube; the cork is dried on the sand-bath immediately before the apparatus is mounted.

The solution of potash employed in the bulb tube *f*, should have a sp. gr. of from 1·25 to 1·27, and must be renewed for every experiment; the portions that have been used may be put aside, and afterwards, when sufficient has been collected, may again be rendered caustic in the usual way by means of quicklime. To the free end of the potash bulbs a tube *h*, filled with fragments of hydrate of potash, is adjusted by means of a cork; this is weighed with the bulbs, and is employed to dry the nitrogen and other gases which escape during the course of the analysis.

The compound commonly used for supplying oxygen to the substance burned is oxide of copper; this oxide readily imparts oxygen to combustible matter in contact with it, but when heated alone, it bears a very high temperature without being decomposed. It is best procured by dissolving copper in pure nitric acid, evaporating to dryness and decomposing the nitrate by heating it strongly in an earthen crucible. Ignition is to be kept up till red fumes cease to appear; if the heat be too great the oxide becomes agglutinated, and requires strong pounding in an iron mortar to pulverise it. The powdered oxide is afterwards sifted through a fine copper sieve, and secured in stoppered glass bottles.

Immediately before each analytical operation, a sufficient quantity of this oxide is to be ignited in a crucible, and while still hot, transferred to a dry tube, by plunging the mouth of the tube into the oxide in the crucible, and then shaking it in piecemeal. The tube is then to be immediately closed with a dry cork, and allowed to cool. Meantime the interior of the retort is to be completely dried by heating each portion of it in succession in the flame of a gas or spirit-lamp, beginning at the closed end, and drawing air through the heated tube by means of a narrower tube passed down just beyond the heated part, and exhausting by the mouth. When every part has thus been dried, the retort is to be corked and allowed to cool.

Five or six grains of the substance to be analysed, powdered and dried, are to be put into a perfectly dry test tube, and this tube with its contents very accurately weighed; its contents are then to be mixed with oxide of copper in a mortar, and the empty tube again weighed; the difference gives the weight of the substance employed. Much caution is requisite in charging the retort. The mortar having been first made dry and warm, is to be placed on a sheet of glazed paper, and first cleared out with a little of the dried oxide of copper, which is thrown aside. Oxide of copper to the depth of an inch is to be poured into the combustion tube; after which a small quantity of the oxide is to be put into the mortar, then the substance to be analysed, then more oxide: the mixture must be made quickly and carefully, adding so much oxide as shall be sufficient to fill a little more than half the retort tube; the mortar is then to be taken in the palm of the left hand, and the mixture introduced, carefully picking it up piecemeal by the retort tube itself; fresh portions of oxide are to be rubbed in the mortar to clear out the last traces of the mixture, and the retort is then to be filled up with pure oxide of copper to within two inches of the extremity.

The proportions of the mixture are represented in fig. 328: the portion from the tail of the tube to the letter *a* consists of pure oxide of copper, from *a* to *b* of the mixture, from *b* to *c* of the rinsings of the mortar, and from *c* to within an inch of the cork is also pure oxide. The tube having been closed by a cork is to be struck smartly in a horizontal position on the table, to clear the tail-like prolongation, and to make an air-way above the oxide from end to end.

The drying tube *e* having been accurately weighed, is next to be fitted to the dried perforated cork, and connected by it air-tight to the retort tube, *a, b, c*; this is now to be placed in the furnace; the potash apparatus, *f*, also previously weighed, is attached to the drying tube by means of a connecting piece of caoutchouc, taking care that the largest bulb is on the arm connected with the drying tube; the potash apparatus should be slightly inclined by placing a cork under the end of the horizontal portion nearest the open extremity. Matters being thus arranged, the next process is to ascertain if the whole be tight, and for this purpose the air in the large bulb is to be gently heated so as to expel a few bubbles; if, on cooling, the liquid rise in the limb and maintain its elevation steadily for a few minutes, the combustion may safely be begun. Charcoal broken into pieces about the size of a walnut is to be ignited, and applied to the portion of the tube nearest the cork, where the pure oxide of copper lies: the action of the heat is limited by a double sheet-iron screen which fits into the furnace, and has a central slit which allows it to bestride the tube; this screen can by degrees be moved further and further down the furnace until the whole tube is heated. An additional screen of single iron plate is hung over the closed end of the furnace to protect the cork, care being taken that the heat never rises so high as to scorch it, or falls so low as to allow of the condensation of moisture in the portion of the retort which projects from the furnace.

When the fore part of the retort is red-hot and the escape of air due to expansion has ceased, about an inch more of it may be heated; and in this way the fire is gradually carried down. At first but a small portion of the gas is absorbed, but when the substance is fairly undergoing decomposition, and the atmospheric air in the apparatus has been expelled, the gas is almost entirely taken up by the potash-ley. When the whole tube is ignited, the heat must be continued till bubbles are no longer disengaged; the potash-ley will now gradually recede into the large bulb; when this is observed to commence, the charcoal must be removed from the tail of the tube; and as soon as the solution of potash has risen sufficiently to fill half the large bulb, the tip of the tail must be nipped off; gentle suction is then to be effected by means of a tube of vulcanized caoutchouc, which is to be fitted to the free extremity of the potash apparatus, and air drawn through the combustion tube by the mouth, in order to displace the carbonic acid and aqueous vapour which the apparatus contains. Dumas prefers to connect the extremity of the retort with a drying tube, and this again with a receiver containing oxygen, which gas is carefully driven over the contents of the tube in the manner shown in fig. 244, part ii. This renders the operation somewhat more complicated, but it is unquestionably more exact, especially for compounds where the proportion of carbon is great. The tube for supplying oxygen is easily adjusted to the retort by drawing out the tail horizontally instead of obliquely, and fitting it on by a caoutchouc connector, care being taken to screen the junction from the influence of heat.

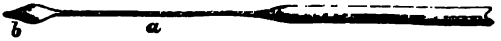
The apparatus is now to be dismounted, and allowed to cool: in about an hour the drying tube *e* may be weighed; one-ninth of the gain which it has experienced indicates the quantity of hydrogen contained in the compound analysed; the potash apparatus, *f*, is also to be weighed, and three-elevenths of what it has gained shows the quantity of carbon. The deficiency is reckoned as oxygen.

The oxide of copper used in these experiments may again be rendered serviceable by moistening it with nitric acid, and igniting it as before.

2. *Analysis of a liquid not containing nitrogen.*

(905) If the liquid be *volatile*, a piece of tube rather less than a quarter of an inch in diameter is to be heated in the blowpipe flame, and drawn out into a capillary portion, *a*, (fig. 329,) about four inches long: about a quarter of an inch below this the tube is to be sealed,

FIG. 329.



and the little piece of tube, *b*, thus left connected with the capillary part, heated and blown into a small bulb about as big as a good-sized pea; this is to be cut off, leaving a capillary neck of about two inches long. Having made a sufficient number of these small bulbs, two of them, which it has been ascertained will freely enter the combustion-tube, are to be accurately weighed; a little of the liquid to be analysed is to be put into a small tube, and the capillary neck of the bulbs inverted into the liquid; the bulbs are then to be warmed by the flame of a spirit-lamp, so that on cooling they shall be about three-fourths filled with the liquid. The necks are now to be sealed by the blowpipe-flame, and the bulbs again weighed; the increase of weight gives the quantity of the liquid which has entered, and which is to be analysed. The oxide of copper having been heated, and allowed to cool with the usual precautions, about an inch and a half of the retort is to be filled with pure oxide; next a file is to be drawn across the capillary neck of one of the bulbs, and the bulb having been placed in the retort, the neck is to be broken by pressure against the glass, and the broken portion of the neck to be dropped in with the bulb; dried oxide of copper is then to be poured in to the depth of two inches more; the second bulb is to be introduced in the same manner as the first, and the tube is to be filled up with oxide; after which it is to be corked and struck smartly on the table as before, to secure free air-way. The combustion-tube is now to be adjusted in the furnace as before, and the first half of the tube is to be gradually heated; when this is red-hot, the liquid must be volatilized by cautiously approximating a piece of ignited charcoal to the part of the tube where the first bulb lies, taking especial care not to heat the tube too much; when by degrees all the liquid in the first bulb has been expelled, the other is to be proceeded with in like manner; the whole tube is finally to be heated carefully, and the gases are to be swept out of the apparatus in the manner already described.

Substances which contain a great excess of carbon sometimes escape complete combustion by the above process; when this is feared, the plan of Dumas, already mentioned, may be adopted; or some finely pulverized, carefully dried chlorate of potash, may be mixed with about four times its weight of oxide of copper, and the portion of the retort near *a* may be filled with it for about an inch; the tail-like prolongation may in this case be dispensed with: at the close of the operation, instead of sucking air through the apparatus, heat is to be very cautiously applied to the chlorate; by this means oxygen is evolved; this burns the last traces of carbon and displaces the gas and aqueous vapour contained in the tubes. The heat must not be too suddenly applied, or a portion of the chlorate is apt to be carried forward mechanically, a circumstance which constitutes the chief objection to its use.

In some cases *chromate of lead* may be advantageously substituted for oxide of copper with substances difficult of combustion, since by a bright red heat alone it gives off a portion of its oxygen.

It is easily prepared by precipitating the chromate or bichromate of potash with a solution of acetate of lead. It should be well washed and heated to incipient fusion before it is used for analysis. It has the advantage of being much less hygroscopic than the oxide of copper. In some cases it may be mixed with bichromate of potash, which parts with oxygen by heat more freely than the lead salt.

3. *Analysis of a body containing nitrogen.*

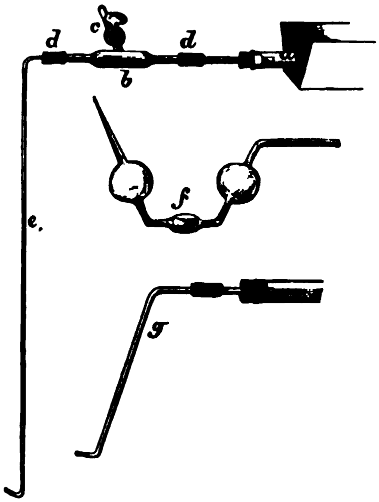
(906) The presence of nitrogen in an organic compound is ascertained by mixing a small quantity of it with a portion of hydrate of potash, and heating it in a small test tube: vapours of ammonia will be evolved if nitrogen be present. Two separate analyses are in this case required; the first, to discover the proportion of carbon and hydrogen; and the second expressly for the nitrogen. When bodies containing nitrogen are burned with oxide of copper, a variable proportion of the lower oxides of nitrogen is formed, which being retained by the chloride of calcium, or by the potash, would render the analysis incorrect. A precaution is therefore employed which renders it necessary to make use of a retort-tube somewhat longer than common; this tube is to be charged as usual to within 4 inches of the opening, and then filled up with clean copper turnings; the apparatus is to be arranged as before directed, the copper turnings brought to full redness, and the analysis is to be cautiously conducted in the ordinary manner. As the oxides of nitrogen pass slowly over the ignited copper they are decomposed, the oxygen combining with the copper, while pure nitrogen escapes: the quantity of carbon and hydrogen is determined exactly in the manner previously described.

(907) *Method of Varrentrapp and Will.*—The most accurate method for ascertaining the proportion of nitrogen is that devised by Varrentrapp and Will; the fundamental fact upon which this method is based, consists in the observation of Gay Lussac, that when azotised matters are heated with a large excess of hydrate of potash or of soda, the whole of the nitrogen is expelled in the form of ammonia. In order to render it available for the purposes of analysis, the subjoined precautions are requisite.

A mixture of two parts of quicklime and one of hydrate of soda is prepared by slaking some well-burned lime with the necessary quantity of a solution of soda; the whole is evaporated to dryness and ignited; the dry mass is pulverized as quickly as possible, and then transferred to well-closed bottles, in order to exclude carbonic acid and moisture. The substance is then mixed in a warm mortar, with alkalized lime instead of with oxide of copper: the accidental presence of a little moisture, after the weight of the material for analysis has been accurately determined, is of no consequence in this case.

Having introduced the mixture into the retort tube, it is better to plug the aperture loosely with a few fibres of asbestus (which has been ignited just before) to prevent any mechanical transport of the mixture into the apparatus through which the gases are passed; on applying heat to the combustion-tube in the ordinary way, and with the usual precautions, the substance is decomposed, and the whole of the nitrogen escapes as ammonia. The drying tube and potash apparatus are dispensed with, and the ammonia is collected by attaching a bulb-tube of the form represented at *f*, fig. 330, air tight, with a good cork to the retort-tube, *a*; the bulbs *f* having been previously charged with hydrochloric acid, (sp. gr. 1·1.) Pure hydrochloric acid is easily procured for this purpose by diluting the ordinary acid of the shops till it has a sp. gr. of 1·1, and distilling it in glass vessels; the first eighth may be rejected, and the distillation proceeded with until three-quarters of the acid employed have passed over. It is better for the operator always to rectify his own acid, in order to be quite sure of the absence of any trace of ammonia. The tube connecting the bulbs should be somewhat larger in diameter than that of the ordinary potash apparatus, in order to allow the liquid to be poured out readily. When the operation is complete, absorption will take place, and the liquid will rise in the bulb nearest the fire; at this moment the tail of the combustion-tube should be nipped off, and air carefully drawn through the apparatus in the usual way. When the combustion has terminated, the contents of the bulb-tube are to be emptied into a small evaporating dish, and the bulbs washed out first with a mixture of alcohol and ether, and afterwards

Fig. 330.



several times with water; some solution of bichloride of platinum is to be added, and the whole evaporated to dryness in a water-bath or a chloride of calcium bath; when dry, it is to be digested with a mixture of two parts of alcohol, sp. gr. 0·833, and one of ether, which dissolves the excess of bichloride of platinum, and leaves the double chloride of platinum and ammonium in a crystalline form. This must now be brought upon a weighed filter, and washed repeatedly with the mixture of two parts of alcohol and one of ether until nothing further is taken up; the precipitate and filter must be dried by a water heat, and the weight accurately observed: 220·52 grs. of the ammonia-chloride of platinum are equivalent to 14 grs. of nitrogen. Instead of collecting the ammonia in hydrochloric acid, it may be condensed in a certain volume of dilute sulphuric acid of known strength (about 150 grains of an acid of which 100 grains will neutralize 2·5 grains of ammonia, will answer the purpose). The acid liquor is then to be washed out of the bulb *f*, diluted, and carefully neutralized by a solution of caustic soda, the strength of which has been accurately graduated.

(908) *Method of Dumas.*—The foregoing method of determining nitrogen answers for all cases excepting those in which it occurs in the form of nitric acid, when it must be determined by volume, and its weight thence deduced. For this purpose the process of Dumas is the most trustworthy:—A retort tube of about twenty inches long is employed, not drawn out into a tail, but sealed with a rounded extremity; about two inches of the tube are filled with bicarbonate of soda, and then the mixture with oxide of copper is added and covered as usual with a layer of pure oxide; beyond this the last two or three inches of the tube are filled with clean copper turnings, as already directed, with a view of decomposing any of the oxides of nitrogen which may be formed. The retort tube is then connected with a three-legged apparatus of brass or copper (Fig. 330, *b*), one limb of which is furnished with a stop-cock, *c*. The connexion with the retort tube *a* is best made by passing a piece of glass tubing through a cork fitting accurately into the mouth of the tube *a*, and connecting the brass apparatus to this small glass tube by a caoutchouc connector, *d*; the third limb is fastened by a similar joint to a glass tube *e*, bent at right angles near one end, with a straight portion upwards of thirty inches long, the other extremity of which is turned up at an acute angle for the convenience of safely delivering the gas: this tube is placed in a vertical direction with its lower upturned

extremity dipping into a small mercurial trough; the stop-cock tube, *c*, is connected with an exhausting syringe, by which a vacuum is produced; the apparatus is left for half an hour to ascertain that all the joints are tight: if the mercury after this lapse of time still stands at the same level, the experiment may be proceeded with, and a moderate heat is applied by a spirit lamp at the end of the retort containing the bicarbonate; by this means carbonic acid is set free and displaces the last portions of air; the exhaustion and the disengagement of gas are repeated alternately three or four times, care being taken to leave sufficient bicarbonate undecomposed to renew this expulsive process at the termination of the experiment. The stop-cock, *c*, is now closed, the air-pump is removed, and a graduated jar containing some solution of potash is inverted in the mercury over the recurved extremity of the long glass tube. The copper turnings are then brought to redness in the usual way by means of a charcoal fire, the decomposition being caused to take place less rapidly than usual. When the part of the retort containing the matter for analysis is red-hot through its entire extent, heat is gradually applied to the carbonate at the end, and the last portions of gas furnished by the combustion are driven into the receiver by the carbonic acid disengaged from the bicarbonate of soda.

Since the products of the combustion are only water, carbonic acid, and nitrogen, the two former are retained by the solution of potash, whilst the latter alone presents itself for measurement. When the apparatus by standing for an hour or two has reached the temperature of the atmosphere, the height of the barometer and thermometer must be carefully noticed; and since the gas will be saturated with moisture, its volume must be corrected by the known methods for the three points of temperature, pressure, and moisture: then, since 100 cubic inches of nitrogen at 60° F. and under a pressure of thirty inches of mercury weigh 30·15 grains, the weight of the nitrogen that a given quantity of the matter analysed contains is easily determined. In this process, as in every case where the proportion of nitrogen alone forms the object of the experiment, after the weight of the material for analysis has been once accurately determined, it is evident that there is nothing to fear from a slight absorption of moisture.

(909) Occasionally the quantity of nitrogen, where large, is advantageously determined by making the combustion just as though we were going to ascertain the proportion of carbon and hydrogen; but, instead of condensing the carbonic acid and

[illegible] the whole of the gases produced are collected over mercury. A bent gas-delivering tube *g*, Fig. 330, is substituted for the usual apparatus for the absorption of water and carbonic acid. In this case it is best to begin at the closed extremity of the tube, and having expelled the atmospheric air by a portion of gas generated from the substance, to collect the rest of the gaseous products in a graduated jar; by agitating the gas with a solution of potash the proportion of nitrogen to the carbon is at once determined, since equal volumes of carbonic acid and nitrogen gas represent single equivalents of carbon and nitrogen. It is not necessary in this case to determine accurately the quantity of material acted upon.

Experience has shown that in the preceding process for organic analysis, the quantity of hydrogen deduced from it is always slightly in excess, usually about [illegible] parts in 100, whilst, unless chromate of lead or chlorate of potash be employed, the carbon is sometimes deficient to the same extent. A deficiency of carbon also occurs if the ash contain alkaline or earthy carbonates.

(910. *Determination of Sulphur and of Phosphorus.*—One of the methods employed for ascertaining the amount of unoxidized sulphur in an organic compound, consists in mixing the substance for analysis with 10 parts of nitre, 2 of dried carbonate of soda, and 30 of pure chloride of sodium, and heating the mass to redness in a tube of hard glass. The sulphur is thus converted into sulphuric acid, which enters into combination with a portion of the alkali. The object of adding the chloride of sodium is simply to moderate the violence of the deflagration. The residue is to be dissolved in water, rendered slightly acid with hydrochloric acid, and the sulphuric acid precipitated by the addition of chloride of barium. If phosphorus be present, it will remain in the acid liquor in the form of phosphoric acid. Its amount may be determined by adding sulphuric acid to throw down the excess of baryta, filtering, supersaturating with ammonia, and adding an ammoniacal solution of sulphate of magnesia; the phosphoric acid is precipitated as the double phosphate of magnesia and ammonia, and is to be collected and ignited in the usual manner. When a large quantity of sulphur is present, part of it becomes converted during the process of combustion with oxide of copper into sulphurous acid, which would be condensed with the carbonic acid, and would thus occasion an error in the determination of the carbon. This source of error may be avoided by interp[illegible] ort tube filled with per- [illegible] of calcium and the oxide of lead between the [illegible]

potash bulbs; the sulphurous acid is then arrested and converted into sulphuric acid, and is retained as sulphate of lead; PbO_2+SO_2 becoming PbO, SO_3.

(911) *Determination of Chlorine, Bromine, and Iodine.*—When the quantity of chlorine, or of any other halogen is to be estimated, the substance for analysis is to be mingled with about 10 times its weight of lime, and is introduced into a tube of Bohemian glass 10 or 12 inches long, and sealed at one end. The tube is to be filled up with fragments of pure lime, which is gradually brought to a red heat, commencing at the open extremity. When the combustion is complete the tube is corked, its outer surface cleared from ashes, and whilst still hot it is plunged into a beaker of cold water. It is thus cracked, and its contents are then treated with nitric acid, and the chlorine, iodine, or bromine is precipitated from the filtered liquid by means of nitrate of silver.

(912) *Calculation of the equivalent of an organic body.*—We will suppose the labour of analysis thus brought to a successful issue. It is evident that the information derived from this source alone is but scanty, for it furnishes no idea either of the number of equivalents of each element entering into the composition of an organic body, or of its relations to the substances concerned in its production or obtainable from it by its decomposition. Whenever it is possible, the equivalent or combining proportion of the compound must be determined. This is effected by preparing a compound of the body with some substance the equivalent of which is well known, and proceeding to analyse the new product. If the organic substance be soluble in water, and capable of entering into combination with oxide of silver, this oxide is for many reasons to be preferred. Oxide of silver combines with many organic bodies, and forms with them compounds insoluble or but sparingly soluble in water; and they may generally be formed by double decomposition, and washed from all adhering impurities. Supposing a silver compound to have been prepared in a state of purity, 15 or 20 grains of it are to be accurately weighed in a counterpoised porcelain crucible. It is then to be carefully incinerated till pure silver alone remains. On again weighing, the loss will give that of the body combined with the silver, and in addition that of one equivalent of oxygen expelled from the oxide of that metal at a red heat. The residual silver should be soluble without remainder in nitric acid. From the weight of the metallic silver, the equivalent number of the organic body that had combined with it may be readily calculated.

An example will best explain the method of proceeding:—

48·73 grs. of acetate of silver left
31·49 grs. of metallic silver.

———

17·24 will therefore express the loss, due to the united weight of acetic acid and oxygen combined with silver; then

$$31{\cdot}49 : \left\{\begin{matrix}\text{1 eq. silver.}\\ 108\end{matrix}\right. :: 17{\cdot}24 : x\ (=59)$$

$$59 - \left\{\begin{matrix}\text{1 eq. oxygen.}\\ 8\end{matrix}\right. = 51,$$ the equivalent number of acetic acid.

Another example will show the method of calculating the number of equivalents of each element in the compound:—

By combustion with oxide of copper it is found that 10 grs. of acetate of silver yield

		Grains.	
5·277 grains of carbonic acid	=	1·439	carbon
1·620 grains of water	=	0·180	hydrogen
And (from previous expt.) .		6·462	silver
The deficiency	=	1·919	oxygen.
		10·000	

Then by proportion—

Silver.		Eq. silver.				
6·462	:	108	: :	Carbon. 1·439	:	x (=24), or C_4.
6·462	:	108	: :	Hydrogen. 0·180	:	x (= 3), or H_3.
6·462	:	108	: :	Oxygen. 1·919	:	x (=32), or O_4.

Total . . . . . . =59
deduct 1 equivalent of oxygen . . 8

and we obtain the equivalent of anhydrous acetic acid . . . } 51, or $C_4H_3O_3$

In some cases the required compound with silver cannot be obtained: a salt of lead is then, if practicable, substituted for it. The residue after incineration in this case does not consist entirely of metallic lead, neither is it all oxide of lead. In order to determine the proportion of each, the residue is carefully weighed and treated with acetic acid in the crucible itself; the oxide of lead is thus dissolved and washed away. When the contents of the crucible have been carefully dried, a second weighing gives the quantity of metallic lead, whilst the loss furnishes that of the oxide. From the metal the quantity of oxide to which it is equivalent may be calculated; this added to the portion dissolved by acetic acid furnishes the whole quantity of oxide contained in the compound: a calculation similar to that employed for the silver salt, then supplies the equivalent number of the body analysed. This method is not quite so accurate as the preceding; it involves more manipulation, and the compounds of lead are apt to undergo slight loss by volatilization at a high temperature.

It would be out of place here to enter in detail into the methods of checking the correctness of an analysis in its various parts. For information upon this point the reader is referred to Liebig's *Handbook of Organic Analysis*. The subject is an important one, and it is not always sufficiently attended to by those who devote themselves to analytical researches of this description.

Classification of Organic Compounds.

(913) The classification of the immense variety of compounds that are presented to the chemist, either naturally by the organs of the living vegetable or animal, or that are derivable from the bodies so obtained by the employment of chemical reagents, may be effected upon two principles. The first of these, which rests upon analogies of function (according to which bodies are arranged under the heads of acids, bases, &c.), might seem to be the more natural, but the second, which is based on the chemical relations of the different compounds, is the truly philosophical system. The first method of arrangement was the only practicable one in the infant state of the science, and it still presents certain advantages to the student in the early stage of his career; but the second will eventually supersede the former, as it greatly facilitates the important study of the true analogies of the different compounds with each other. The time is approaching when, to use the words of Gerhardt, "organic chemistry, awarding to physical characters and chemical functions but a secondary importance as means of classification, must rest upon some wider principle which is applicable to all substances, whatever may be their physical characters and their chemical functions. After having studied bodies in relation to the metamorphoses of which they are susceptible, *she must group together those which are derived one from the other,* and when she has thus arranged a certain number of groups, or of series, she must inquire whether amongst the bodies which these groups embrace, there be not some which have a higher degree of

and furnish derivative series in which the homology is still preserved. We may exemplify the formation of these collateral series in the derivatives obtained from the alcohols.

2. *Vinic Acids.*—When ordinary alcohol is mixed with an equal weight of strong sulphuric acid, a large portion of the alcohol and of the acid unite and form a new compound acid termed sulpho-vinic or sulph-ethylic acid $HO, C_4H_5O, 2 SO_3$; two equivalents of sulphuric acid uniting with the elements of 1 equivalent of alcohol, whilst two equivalents of water are liberated. Now wood spirit, fousel oil, and each of the other alcohols, when similarly treated furnishes a compound perfectly analogous to sulph-ethylic acid, as is represented in the following table:—

Sulphomethylic Acid	$HO, C_2 H_3 O, 2 SO_3$
Sulphethylic (Sulphovinic) Acid	$HO, C_4 H_5 O, 2 SO_3$
Sulphotritylic Acid	$HO, C_6 H_7 O, 2 SO_3$
Sulphotetrylic Acid	$HO, C_8 H_9 O, 2 SO_3$
Sulphamylic Acid	$HO, C_{10}H_{11}O, 2 SO_3$
&c. &c.	

the general formula for these vinic acids being $[HO, (C_nH_{n+1}) O, 2 SO_3.]$

3. *Ethers.*—If sulpho-vinic acid, or if a mixture of equal volumes of sulphuric acid and of alcohol, be exposed to heat in a retort and distilled, a volatile liquid which has been long known under the name of *ether* passes over; and a similar body may be obtained from the other alcohols. The composition of these different bodies is such that they all admit of being represented by formulæ which contain the same elements as the alcohols which yield them, minus 1 equivalent of water, thus:—

	$(C_nH_{n+1})O$		$(C_nH_{n+1}O, + C_nH_{n+1}O)$
Methylic Ether	$C_2 H_3 O$	or	$2 (C_2 H_3 O)$
Vinic (or ordinary) Ether .	$C_4 H_5 O$	or	$2 (C_4 H_5 O)$
Propylic (Tritylic) Ether . .	$C_6 H_7 O$	or	$2 (C_6 H_7 O)$
Butylic (Tetrylic) Ether . .	$C_8 H_9 O$	or	$2 (C_8 H_9 O)$
Amylic Ether	$C_{10}H_{11}O$	or	$2 (C_{10}H_{11}O)$

the general formula for these ethers being $(C_nH_{n+1}) O$; consequently they may be regarded as being derived from the alcohols by the abstraction of 1 equivalent of water; for instance—

$$\overbrace{C_4H_5O, HO}^{\text{Alcohol.}} - HO = \overbrace{C_4H_5O,}^{\text{Ether.}}$$

or generally $[(C_nH_{n+1}) O, HO]—HO = (C_nH_{n+1}) O$. It is, however, more probable, as will be shown hereafter (986), that they are formed not from 1 equivalent, but from 2 equivalents of alcohol, by the removal of 2 equivalents of water; $2\ [(C_nH_{n+1})\ O, HO] - 2\ HO = 2\ [(C_nH_{n+1})\ O.]$

4. *Hydriodic and other corresponding Ethers.*—The ethers in their turn admit of the displacement of the oxygen which they contain by chlorine, bromine, or iodine, producing a number of bodies analogous to each other. Thus, if alcohol be treated with hydrochloric, hydrobromic, or hydriodic acid, instead of with sulphuric acid, water is separated, and chloride, bromide, or iodide of ethyl is formed: $C_4H_6O_2 + HI = C_4H_5I + 2HO$.

The following table exhibits the analogy and the homology of these compounds:—

	Chloride.	Bromide.	Iodide.
Methyl compounds .	C_2H_3Cl	C_2H_3Br	C_2H_3I
Ethyl do. .	C_4H_5Cl	C_4H_5Br	C_4H_5I
Propyl (Trityl) do. .			
Butyl (Tetryl) do. .	C_8H_9Cl		
Amyl do. .	$C_{10}H_{11}Cl$	$C_{10}H_{11}Br$	$C_{10}H_{11}I$
&c.	&c.	&c.	&c.

In the preceding table several blank spaces appear, the compounds corresponding to them not having been formed as yet, though there is no doubt that they could be obtained without difficulty.

5. *Hydrocarbon radicles of the Ethers.*—When iodide of ethyl is sealed up in a strong tube and heated to about 300° F., in contact with metallic zinc, iodide of zinc and a quantity of a peculiar hydrocarbon (C_4H_5) is set at liberty. This substance has been termed *ethyl*, and has been regarded as the basis of ether, which has the composition of an oxide of this hydro-carbon. By analogous means the radicles of several of the other ethers have also been isolated. The general formula of these compounds may be represented as (C_nH_{n+1}), or as (C_nH_{n+1}, C_nH_{n+1}); thus—

Methyl . . . . $= C_2H_3$ or (C_4H_3, C_2H_3)
Ethyl . . . . $= C_4H_5$ or (C_4H_5, C_4H_5)
Propyl (Trityl) . . . . . . Not isolated
Butyl (Tetryl) . . . . . . $= C_8H_9$ or (C_8H_9, C_8H_9)
Amyl . . . . $= C_{10}H_{11}$ or $(C_{10}H_{11}, C_{10}H_{11})$

6. *Homologous Hydro-carbons of the form* (C_nH_n).—If alcohol be treated with three or four times its volume of sulphuric acid, or with anhydrous phosphoric acid, and be distilled, it loses the elements of two equivalents of water instead of one equivalent

only, and a gaseous compound of carbon and hydrogen, which constitutes olefiant gas, is liberated. A similar hydro-carbon may be obtained from each of the other alcohols: for example—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} - 2\ HO = \overbrace{C_4H_4}^{\text{Oleft. Gas.}};$$

and generally,

$$(C_nH_{n+2})\ O_2 - 2\ HO = (C_nH_n)$$

	C_nH_n	or	$(C_nH_{n-1})\ H$
Methylene	$C_2\ H_2$	or	$C_2\ H,\ H$
Ethylene (Olefiant Gas)	$C_4\ H_4$	or	$C_4\ H_3,\ H$
Propylene (Tritylene)	$C_6\ H_6$	or	$C_6\ H_5,\ H$
Tetrylene (Oil Gas)	$C_8\ H_8$	or	$C_8\ H_7,\ H$
Amylene	$C_{10}H_{10}$	or	$C_{10}H_9,\ H$

7. *Aldehyds.*—If alcohol be distilled with oxide of manganese and dilute sulphuric acid, or with other oxidizing agents the oxidating influence of which can be applied with sufficient slowness and regularity, a very volatile liquid may be obtained (971), which contains the elements of alcohol, minus 2 equivalents of hydrogen. This substance is known as aldehyd. By similar means corresponding compounds may be obtained from the other alcohols, these aldehyds possessing the

General Formula.	$(C_nH_n)\ O_2$	or	$HO,\ (C_nH_{n-1})\ O$
Formic Aldehyd	$C_2\ H_2\ O_2$	or	$HO,\ C_2\ H\ O$
Acetic Aldehyd	$C_4\ H_4\ O_2$	or	$HO,\ C_4\ H_3O$
Propionic Aldehyd . . .	$C_6\ H_6\ O_2$	or	$HO,\ C_6\ H_5O$
Butyric Aldehyd (Butyral)	$C_8\ H_8\ O_2$	or	$HO,\ C_8\ H_7O$
Valeric Aldehyd (Valeral).	$C_{10}H_{10}O_2$	or	$HO,\ C_{10}H_9O$

the action of 2 equivalents of oxygen upon 1 equivalent of an alcohol is to convert it into an aldehyd, with the removal of 2 equivalents of water; thus

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} + O_2 = \overbrace{C_4H_4O_2}^{\text{Aldehyd.}} + 2\ HO;$$

and, generally, $(C_nH_{n+2})\ O_2 + O_2 = (C_nH_n)\ O_2 + 2\ HO$.

8. *Homologous Volatile Acids.*—The aldehyds are neutral substances, but they rapidly absorb 2 equivalents of oxygen from the air, and thus become converted into powerful hydrated acids, the general formula of these hydrates being, $HO,\ (C_nH_{n-1})\ O_3$ or $(C_nH_n)O_4$. These acid compounds are therefore derived by a process of oxidation from the alcohols; the formation of the aldehyd being the intermediate stage in [illegible]ion: 4 equivalents

of oxygen, by acting on 1 equivalent of an alcohol, convert it into one equivalent of the hydrate of a corresponding volatile acid, whilst 2 equivalents of hydrogen are eliminated in the form of water. Thus:—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} + O_4 = \overbrace{C_4H_4O_4}^{\text{Acetic Acid.}} + 2\ HO,$$

and generally

$$C_nH_{n+2}O_2 + O_4 = (C_nH_n)\,O_4 + 2\ HO.$$

The volatile fatty acids belong to this series, which is indeed more complete than that of the alcohols. A considerable number of these acids exist in many of the vegetable and animal fats and oils; but chemists have not as yet succeeded in obtaining a general method of reconverting the fatty acids into alcohols, though the alcohols are readily converted into their corresponding acids. The more important of these acids are the following:—

General Formula	= HO, $(C_nH_{n-1})\,O_3$	or	$(C_nH_n)\,O_4$
Formic Acid	HO, $C_2\,H\,O_3$	or	$C_2\,H_2\,O_4$
Acetic	HO, $C_4\,H_3\,O_3$	or	$C_4\,H_4\,O_4$
Propionic	HO, $C_6\,H_5\,O_3$	or	$C_6\,H_6\,O_4$
Butyric	HO, $C_8\,H_7\,O_3$	or	$C_8\,H_8\,O_4$
Valerianic	HO, $C_{10}H_9\,O_3$	or	$C_{10}H_{10}O_4$
Caproic	HO, $C_{12}H_{11}O_3$	or	$C_{12}H_{12}O_4$
Œnanthylic	HO, $C_{14}H_{13}O_3$	or	$C_{14}H_{14}O_4$
Caprylic	HO, $C_{16}H_{15}O_3$	or	$C_{16}H_{16}O_4$
Pelargonic	HO, $C_{18}H_{17}O_3$	or	$C_{18}H_{18}O_4$
Capric or Rutic	HO, $C_{20}H_{19}O_3$	or	$C_{20}H_{20}O_4$
Lauric	HO, $C_{24}H_{23}O_3$	or	$C_{24}H_{24}O_4$
Myristic	HO, $C_{28}H_{27}O_3$	or	$C_{28}H_{28}O_4$
Palmitic	HO, $C_{32}H_{31}O_3$	or	$C_{32}H_{32}O_4$
Stearic	HO, $C_{36}H_{35}O_3$	or	$C_{36}H_{36}O_4$
Cerotic	HO, $C_{54}H_{53}O_3$	or	$C_{54}H_{54}O_4$
Melissic	HO, $C_{60}H_{59}O_3$	or	$C_{60}H_{60}O_4$

Each equivalent of acid corresponds to 4 volumes of vapour, and requires 1 equivalent of base for its saturation.

This group of acids, which is one of the most complete of the homologous series, illustrates in a very interesting manner the general similarity in properties which always exists in homologous bodies. This statement may appear paradoxical when the extreme terms of the series are compared together, since formic acid is an exceedingly pungent corrosive volatile liquid, which requires cooling below 32°, in order to render it solid, and it is miscible with water in all proportions; whilst melissic acid requires a temperature of 192° for its fusion, is insoluble in water, and has the properties of a fat: but if we compare together the contiguous terms of the series, such as the formic with the acetic, the acetic with the propionic acid, and so on, no abrupt change in properties will be perceived between the contiguous terms; each, as the proportion of carbon and hydrogen increases, becomes gradually less and less volatile, less fusible, less inclined to dissolve in water, until we reach the true fatty acids. Now this similarity in properties, which is observed equally in other groups of homologous substances, naturally leads to the supposition that there must be a similarity in chemical constitution. It is not unreasonable to suppose that the acids $HO, (C_nH_{n-1}), O_3$, are all formed upon the plan, or type of the simplest of them, viz., formic acid. Various theories may be advanced as to the composition of formic acid, but whatever that composition may be, we may imagine with Wurtz and with Gerhardt that the other acids are so many varieties of formic

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* *Table to illustrate the arrangem*

Hydro-carbons. (C_nH_n) or $(C_nH_{n-1})H)$	Positive Radicles. (C_nH_{n+1}) or $2(C_nH_{n+1})$	Simple Ethers. $(C_nH_{n+1})O$ or $(C_nH_{n+1}O, C_nH_{n+1}O)$	Sulphides. $(C_nH_{n+1})S$ or $(C_nH_{n+1}S, C_nH_{n+1}S)$	Ch (C
1. C_2H_2	$2(C_2H_3)$	(C_2H_3O, C_2H_3O)	(C_2H_3S, C_2H_3S)	C_2
2. C_4H_4	$2(C_4H_5)$	(C_4H_5O, C_4H_5O)	(C_4H_5S, C_4H_5S)	C_4
3. C_6H_6				
4. C_8H_8	$2(C_8H_9)$	(C_8H_9O, C_8H_9O)		C_8
5. $C_{10}H_{10}$	$2(C_{10}H_{11})$	$(C_{10}H_{11}O, C_{10}H_{11}O)$	$(C_{10}H_{11}S, C_{10}H_{11}S)$	C_{10}
6. $C_{12}H_{12}$	$2(C_{12}H_{13})$			
7.				
8. $C_{16}H_{16}$				C_{16}
9. $C_{18}H_{18}$				
10. $C_{20}H_{20}$				
11.				
12.				
13.				
14.				
15.				
16. $C_{32}H_{32}$		$(C_{32}H_{33}O, C_{32}H_{33}O)$	$(C_{32}H_{33}S, C_{32}H_{33}S)$	C_{32}
17.				
18.				
19.				
20.				
27. $C_{54}H_{54}$				
30. $C_{60}H_{60}$				
Relation to Hydrogen	H or $\begin{matrix}H\\H\end{matrix}\Big\}$	HO or $\begin{matrix}HO\\HO\end{matrix}\Big\}$	HS or $\begin{matrix}HS\\HS\end{matrix}\Big\}$	HC

id, which contain ethyl, trityl, tetryl, &c., instead of hydrogen ; us :—

Formic Acid	$HO, C_2(H)O_3$
Acetic, or Methylformic	$HO, C_2(C_2H_3)O_3$
Propionic, or Ethylformic	$HO, C_2(C_4H_5)O_3$
Butyric, or Tritylformic	$HO, C_2(C_6H_7)O_3$
Valerianic, or Tetrylformic	$HO, C_2(C_8H_9)O_3$

somewhat similar hypothesis might be extended to the different cohols themselves.

It will be perceived that all these groups, derived from the cohols by decomposition, are produced by an analogous decom- sition of the several alcohols, and that they all preserve a strict mology in their respective groups. This will be more easily aced by the aid of the table below,* in which the different asses of compounds just described are so arranged that all those mpounds which are placed in the same vertical column are

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unds in Homologous Series.

s. O_2 $HO)$	Mercaptans. $(C_nH_{n+2})S_2$ or $(C_nH_{n+1}S, HS)$	Aldehyds. $(C_nH_n)O_2$ or $(C_nH_{n-1})O, HO$	Volatile Acids. $(C_nH_n)O_4$ or $HO, (C_nH_{n-1})O_3$	Compound Ethers. $C_nH_{n+1}O, C_nH_{n-1}O_3$	
HO	C_2H_3S, HS	$C_2H\ O, HO$	$HO, C_2H\ O_3$	$C_2H_3O, C_2H\ O_3$	1.
HO	C_4H_5S, HS	C_4H_3O, HO	$HO, C_4H_3O_3$	$C_4H_5O, C_4H_3O_3$	2.
HO		C_6H_5O, HO	$HO, C_6H_5O_3$	$C_4H_5O, C_6H_5O_3$	3.
HO		C_8H_7O, HO	$HO, C_8H_7O_3$	$C_4H_5O, C_8H_7O_3$	4.
HO	$C_{10}H_{11}S, HS$	$C_{10}H_9O, HO$	$HO, C_{10}H_9O_3$	$C_{10}H_{11}O, C_{10}H_9O_3$	5.
HO		$C_{12}H_{11}O, HO$	$HO, C_{12}H_{11}O_3$	$C_4H_5O, C_{12}H_{11}O_3$	6.
		$C_{14}H_{13}O, HO$	$HO, C_{14}H_{13}O_3$	$C_4H_5O, C_{14}H_{13}O_3$	7.
HO			$HO, C_{16}H_{15}O_3$	$C_4H_5O, C_{16}H_{15}O_3$	8.
			$HO, C_{18}H_{17}O_3$	$C_4H_5O, C_{18}H_{17}O_3$	9.
		$C_{20}H_{19}O, HO$	$HO, C_{20}H_{19}O_3$	$C_4H_5O, C_{20}H_{19}O_3$	10.
					11.
HO			$HO, C_{24}H_{23}O_3$	$C_4H_5O, C_{24}H_{23}O_3$	12.
					13.
			$HO, C_{28}H_{27}O_3$	$C_4H_5O, C_{28}H_{27}O_3$	14.
					15.
HO	$C_{32}H_{33}S, HS$	$C_{32}H_{31}O, HO$	$HO, C_{32}H_{31}O_3$	$C_{32}H_{33}O, C_{32}H_{31}O_3$	16.
					17.
			$HO, C_{36}H_{35}O_3$	$C_4H_5O, C_{36}H_{35}O_3$	18.
					19.
			$HO, C_{40}H_{39}O_3$		20.
HO			$HO, C_{54}H_{53}O_3$	$C_{54}H_{55}O, C_{54}H_{53}O$	27.
HO			$HO, C_{60}H_{59}O_3$		30.
$\left.\begin{matrix}O\\O\end{matrix}\right\}$	$2\ HS$ or $\left.\begin{matrix}HS\\HS\end{matrix}\right\}$				

homologous, whilst those which are placed in different colum are heterologous, or dissimilar in molecular constitution and i chemical characters: but it will be seen that those bodies in th same horizontal line are all related to the same alcohol; they a all formed from it by reactions similar to those by which each o the corresponding compounds in the other horizontal lines a formed from their alcohol.

Exceptions to this uniformity occur in the last column, in th case of the compound ethers, the formula for which, in the majorit of instances represents the ether formed by the union of the aci with ethylic ether, since these compounds have been more generall formed and studied than any other kind of compound ethe; though in a few instances the compound ether resulting from th union of the acid of the series with its corresponding ether, i given, and there can be no doubt that such ethers might in a cases be formed if any sufficient inducement to their preparati existed; or if the materials required were sufficiently abundant.

The column headed *Mercaptans* contains a series of compounds which correspond to the alcohols, and are strictly analogous to them; they contain sulphur in the place of oxygen: the sulphides are analogous in like manner to the ethers; and the bromides and iodides, which however are not included in the table, are analogous to the chlorides. The quantities represented by the formulæ given in the table yield in all cases where the compounds are volatile without decomposition, 4 volumes of vapour. In this table many blanks occur, which could in most cases be filled up if the compounds which correspond to them presented sufficient interest to induce the chemist to prepare them. New compounds are indeed being continually added to the list. By thus mapping out the territory which has been explored, the progress of future research is materially aided, and each new compound, as soon as discovered, more readily falls into its true place, and its relations to other bodies previously known are anticipated, and readily verified.

[illegible] *Theory of Compound Radicles.*—Liebig explains the community of properties between the terms of homologous series by supposing the existence, in each, of a certain group of elements which he supposes to be the nucleus of the series. He has, in fact, made the theory of compound radicles, as it is termed, the basis of his classification, and has defined organic chemistry to be the chemistry of compound radicles. According to this supposition, the [illegible] hydr[illegible] all the *heterolo-*

gous bodies of the series, or bodies not analogous in composition, are derived : for example,

Compound Radicle.		*Ether, or Oxide of the Radicle.*	
Methyl . . .	$(C_2 H_3)$	Methylic Ether .	$(C_2 H_3)$, O
Ethyl	$(C_4 H_5)$	Vinic Ether . .	$(C_4 H_5)$, O
Amyl	$(C_{10} H_{11})$	Amylic Ether .	$(C_{10} H_{11})$, O

Alcohol, or Hydrated Oxide.		*Compound Ether.*	
Wood Spirit	$(C_2 H_3)$ O, HO	Formiate of Methyl .	$(C_2 H_3)$ O, $(C_2 H) O_3$
Alcohol . .	$(C_4 H_5)$ O, HO	Acetate of Ethyl . .	$(C_4 H_5)$ O, $(C_4 H_3) O_3$
Fousel Oil .	$(C_{10} H_{11})$O, HO	Valerate of Amyl . .	$(C_{10} H_{11})$O, $(C_{10} H_9) O_3$

Upon this theory the simple ethers are oxides of the peculiar electro-positive hydrocarbon which forms the radicle of the series; the alcohols are the hydrated oxides of the same radicle, and the so-called hydrochloric, hydrobromic, hydriodic, and hydrosulphuric ethers, are simply compounds in which chlorine, bromine, iodine, or sulphur have taken the place of the oxygen of the ordinary ether, just as in the compounds of a metal the chlorine, the iodine, or the sulphur, displaces the oxygen; whilst the compound group termed ethyl (C_4H_5) discharges a function in these compounds analogous to that of potassium in its salts: thus, calling ethyl (C_4H_5) = Et., the two series would run as follows :—

Oxide of potassium	KO	Oxide of ethyl .	EtO
Chloride of ditto .	KCl	Chloride of ditto .	EtCl
Iodide of ditto .	KI	Iodide of ditto .	EtI
Sulphide of ditto .	KS	Sulphide of ditto .	EtS

The mercaptans correspond in composition to alcohol in which the place of the oxygen is supplied by sulphur; whilst the compound ethers, such as the formic, the acetic, and the valeric, are regarded in the light of salts, in which the formic, the acetic, or valeric acid is combined with the oxide of methyl, of ethyl, or other compound radicle, by which its acid properties are completely neutralized.

The aldehyds and acids are regarded as belonging to a different series, which contains a different organic radicle possessed of electro-negative properties : for instance,

Compound Radicle.	Hydrated Oxide, or Aldehyd.		Hydrated Volatile Acid.	Perchloride.
Formyl (C_2H)	Formic Aldehyd } (C_2H)O, HO		Formic HO, $(C_2H)O_3$	Chloro-form } $(C_2H)Cl_3$
Acetyl (C_4H_3)	Acetic Aldehyd } (C_4H_3)O, HO	Aldehydic Acid } HO, $(C_4H_3)O_3$	Acetic HO, $(C_4H_3)O_3$	
Valeryl $(C_{10}H_9)$	Valeric Aldehyd } $(C_{10}H_9)$O, HO		Valeric HO, $(C_{10}H_9)O_3$	

The radicle of each of these electro-negative series, it will be seen, differs from the radicle of the alcohol from which they are produced by 2 equivalents of hydrogen: methyl (C_2H_3) by the loss of 2 equivalents of hydrogen yielding the elements of formyl (C_2H); ethyl minus 2 equivalents of hydrogen, furnishing the elements of acetyl, and so on.

It is true that the theory of compound radicles supposes the existence of a number of substances which have not been isolated, and possibly also of many which can have no separate existence. But this is a disadvantage which, as Dr. Gregory justly remarks, it shares with every chemical theory which has hitherto been broached; and if the view of Liebig does not afford a correct representation of the molecular constitution of organic bodies, it is at least a very convenient fiction, since it materially facilitates the retention of their composition in the memory, and the comprehension of the metamorphoses which such compounds experience. One of the first groups to which it was systematically applied by Liebig and Wöhler was that derived from the essential oil of bitter almonds. This oil was regarded by these chemists as containing an organic radicle, to which they gave the name of benzoyl ($C_{14}H_5O_2$), and which may be conveniently distinguished by the symbol Bz. Although unsuccessful in the attempt to isolate this radicle, they succeeded in transferring the group of which it was supposed to consist, from one elementary substance to another, and in causing it to enter into combination with other organic groups; and by the aid of this hypothesis they were enabled to give as simple and intelligible an account of the mode in which the compounds derived from it were formed, as though they had been dealing with the salts or other compounds of a metal. The advantages thus obtained may be rendered evident by comparing the empirical formulæ of these compounds with those in which the organic radicle is assumed to be present:—

	Empirical Formula.	$C_{14}H_5O_2$=Bz	
Oil of Bitter Almonds .	$C_{14}H_6O_2$	BzH,	Hydride of Benzoyl
Benzoic Acid	$C_{14}H_6O_4$	HO, BzO,	Oxide of Benzoyl
Chlorinated Compound .	$C_{14}H_5O_2Cl$	BzCl,	Chloride of Benzoyl
Sulphur Compound . .	$C_{14}H_5O_2S$	BzS,	Sulphide of Benzoyl
Cyanogen Compound .	$C_{16}H_5O_2N$	BzCy,	Cyanide of Benzoyl

It is, moreover, to be observed that many of the organic radicles may be isolated. The existence of cyanogen as an electro-negative organic radicle, and the remarkable analogy in its mode of combination to chlorine and the halogens, was known long before Liebig had attempted to generalize the theory. Bunsen subsequently isolated kakodyl (C_4H_6As), which is an excellent representative of the electro-positive class of radicles, and others of analogous composition have since been obtained; whilst several bodies having the composition of such radicles as ethyl and methyl, which are supposed to form the bases of the alcohols and ethers, have been obtained in a separate form by the valuable researches of Frankland and others.

(917) *Chemical Types.*—The homologous series of the alcohols which has already been briefly reviewed (914) has its representatives among the simpler compounds contained in the department of inorganic chemistry; for by deducting $2(C_2H_2)$ from methyl and the compounds of the methylic group (contained in the horizontal line 1 in the table), we arrive at hydrogen and some of its most important compounds of simple constitution. Thus methyl, if deprived of $2(C_2H_2)$, would leave a residue consisting only of hydrogen; $2\,(C_2H_3) - 2\,(C_2H_2) = H_2$. Methylic ether deprived of $2(C_2H_2)$ would leave water; $2\,(C_2H_3O) - 2\,(C_2H_2) = 2\,HO$: the residue from chloride of methyl after a similar deduction would be hydrochloric acid, and that of the sulphide of methyl and of methylic mercaptan would be sulphuretted hydrogen. Hence it appears that the radicles methyl, ethyl, trityl, tetryl, amyl, &c., are bodies which correspond to hydrogen, and that they may be regarded as homologues of a series in which hydrogen forms the lowest term; that the simple ethers and alcohols are homologues of water, whilst the chlorides and iodides are homologues of hydrochloric and hydriodic acid, and the sulphides and mercaptans are homologues of hydrosulphuric acid. Water, hydrochloric, and hydrosulphuric acid are, therefore, the patterns or *types* upon which these several bodies are formed.

This idea of referring organic compounds to some simple representative or type has been systematically worked out by Laurent and by Gerhardt.

The four principal types to which the latter chemist refers most of the compounds of organic chemistry are the following:—

1. The metallic or hydrogen type $\left.\begin{matrix}H\\H\end{matrix}\right\}$ or H_2
2. The oxide or water type . . $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$, or $\left\{\begin{matrix}H, O\\H, O\end{matrix}\right.$
3. The chloride or hydrochloric acid type . . . . . . $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$
4. The nitride, or ammonia type . $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$

It is important to remark, that many bodies are referred to the same type, though they present no analogy in chemical properties, either to it or to each other. The various radicles which have been proved or assumed to exist in organic compounds vary in character as much as the elementary bodies themselves. Some, like cyanogen (C_2N), being strongly electro-negative, may be arranged with chlorine, oxygen, and sulphur, on the right hand side of a double converging series; such as the following:—

POTASSIUM. CHLORINE.
SODIUM. OXYGEN.
CALCIUM. SULPHUR.
IRON. GOLD.
&c. &c.
ANTIMONY.
ARSENIC.

whilst others, like aldehyd and acetone, agree with arsenic and antimony in occupying a central or intermediate position; and others, like kakodyl (C_4H_6As) and the metallic derivatives of alcohol would be arranged with the electro-positive bodies, potassium, sodium, calcium, &c., on the left hand side of such a series. When we compare together different compounds belonging to the same series, a progressive change in properties is observed, so that the differences observable between any two such compounds become greater, the wider is the interval between the respective places in the series of the two terms submitted to the comparison. Following this idea to its extreme limits, the same type may therefore comprehend bodies belonging to the three classes of acids, of bases, and of neutral bodies; the acids or electro-negative bodies being at one extremity of the series, and the neutral bodies occupying the intermediate positions, provided that the bases or electro-positive bodies be arranged at the opposite extremity.

The application of these types by Gerhardt to the compounds of organic chemistry will be best understood by means of a few examples:—

1. The hydrogen or metallic type $\left\{\begin{matrix}H\\H\end{matrix}\right.$

To this class Gerhardt refers the radicles of the alcohols, the hypothetical oxidized radicles of certain acids, marsh gas and the hydrocarbons homologous with it, the aldehyds, &c.

Methyl . . . . $\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.$

	Ethyl	$\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.$
	Marsh gas (hydride of methyl) . . .	$\left\{\begin{matrix}C_2H_3\\H\end{matrix}\right.$
	Hydride of amyl	$\left\{\begin{matrix}C_{10}H_{11}\\H\end{matrix}\right.$
Hypothetical	Othyl (Gerhardt's acetyl)	$\left\{\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right.$
	Benzoyl	$\left\{\begin{matrix}C_{14}H_5O_2\\C_{14}H_5O_2\end{matrix}\right.$
	Aldehyd (hydride of othyl)	$\left\{\begin{matrix}C_4H_3O_2\\H\end{matrix}\right.$
	Acetone (methylide of othyl) . . .	$\left\{\begin{matrix}C_4H_3O_2\\C_2H_3\end{matrix}\right.$

2. The type water . $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$, or $\left\{\begin{matrix}H, O\\H, O\end{matrix}\right.$

includes the alcohols, the hydrosulphuric ethers and mercaptans, the simple and compound ethers, the double ethers, the hydrated monobasic acids and their anhydrides: for instance,

Wood spirit . . .	$\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O_2$, or	$\left\{\begin{matrix}C_2H_3, & O\\H, & O\end{matrix}\right.$
Alcohol	$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2$, or	$\left\{\begin{matrix}C_4H_5, & O\\H, & O\end{matrix}\right.$
Hydrosulphuric ether.	$\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}S_2$, or	$\left\{\begin{matrix}C_4H_5, & S\\C_4H_5, & S\end{matrix}\right.$
Mercaptan	$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}S_2$, or	$\left\{\begin{matrix}C_4H_5, & S\\H, & S\end{matrix}\right.$
Ordinary ether . .	$\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2$, or	$\left\{\begin{matrix}C_4H_5, & O\\C_4H_5, & O\end{matrix}\right.$
Amylethylic ether .	$\left.\begin{matrix}C_{10}H_{11}\\C_4H_5\end{matrix}\right\}O_2$, or	$\left\{\begin{matrix}C_{10}H_{11}, & O\\C_4H_5, & O\end{matrix}\right.$
Acetic ether . . .	$\left.\begin{matrix}C_4H_3O_2\\C_4H_5\end{matrix}\right\}O_2$, or	$\left\{\begin{matrix}C_4H_3O_2, & O\\C_4H_5, & O\end{matrix}\right.$
Hydrated acetic acid .	$\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2$, or	$\left\{\begin{matrix}C_4H_3O_2, & O\\H, & O\end{matrix}\right.$
Acetic anhydride . .	$\left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}O_2$, or	$\left\{\begin{matrix}C_4H_3O_2, & O\\C_4H_3O_2, & O\end{matrix}\right.$

3. The hydrochloric acid type $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$ comprehends the ethers of the hydracids, and the oxychlorides of the radicles of the monobasic acids; for example:—

Hydrochloric ether . . . . $\left\{\begin{matrix} C_4H_5 \\ Cl \end{matrix}\right.$

Iodide of amyl . . . . $\left\{\begin{matrix} C_{10}H_{11} \\ I \end{matrix}\right.$

Benzoic oxychloride . . . . . .
(Chloride of benzoyl) . . . . . . $\left\{\begin{matrix} C_{14}H_5O_2 \\ Cl \end{matrix}\right.$

Acetic oxychloride . . . . $\left\{\begin{matrix} C_4H_3O_2 \\ Cl \end{matrix}\right.$

4. The ammonia type $\left.\begin{matrix} H \\ H \\ H \end{matrix}\right\}N$, includes the compound ammonias and the amides:—

Ethylia (ethylamine) . . . . $\left.\left\{\begin{matrix} C_4H_5 \\ H \\ H \end{matrix}\right.\right\}N$

Diphosphethylia . . . . . . $\left.\left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ H \end{matrix}\right.\right\}P$

Trimethylia (trimethylamine) . . . $\left.\left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \end{matrix}\right.\right\}N$

Acetamide . . . . $\left.\left\{\begin{matrix} C_4H_3O_2 \\ H \\ H \end{matrix}\right.\right\}N$

Benzoyl-salicylamide . . . . . . $\left.\left\{\begin{matrix} C_{14}H_5O_2 \\ C_{14}H_5O_4 \\ H \end{matrix}\right.\right\}N$

Many compounds, such as hydrated oxide of ammonium, not included under the preceding types, may be referred to combinations of two of the foregoing types with each other.

It is needful to bear in mind that a body does not necessarily belong to a given type merely because it may contain one of the characteristic elements which contribute to form the typical compound. It would be wrong, for example, to infer that a compound was formed on the hydrochloric acid type simply in consequence of the presence of chlorine among its components; since the properties of a body are dependent not only upon the nature and proportions of its component elements, but also in a very important manner upon the molecular arrangement of those components:—For example, the chlorine in chlorate of potash does not perform the same part that it does in chloride of potassium; in the latter instance it is susceptible of displacement when mixed with nitrate of silver; the soluble nitrate of potash and insoluble chloride of silver being formed when solutions of the two salts are mixed—

$$Ag, NO_6 + KCl = AgCl + K, NO_6$$

whereas, when chlorate of potash and nitrate of silver are mixed, no precipitation of chloride of silver takes place. So it is in organic substances; for example, when isatin $C_{16}H_5NO_6$ (a compound derived from indigo) is distilled with hydrate of potash, a powerful volatile base termed aniline ($C_{12}H_5, H_2N$) is obtained. Now compounds of isatin may be formed in which one, two, and three equivalents of chlorine may be successively substituted for an equal number of equivalents of hydrogen in isatin; and when these compounds are distilled with hydrate of potash, they yield substances corresponding in composition to aniline, but in which a certain number of equivalents of hydrogen are displaced by a corresponding number of equivalents of chlorine, thus:—

$$\overbrace{(C_{16}H_5)NO_4}^{\text{Isatin.}} + \overbrace{4(KO, HO)}^{\text{Hyd. Potash.}} = \overbrace{(C_{12}H_5)H_2N}^{\text{Aniline.}} + \overbrace{4(KO, CO_2)}^{\text{Carb. Potash.}} + 2\,H.$$

$$\overbrace{(C_{16}H_4Cl)NO_4}^{\text{Chlorisatin.}} + 4(KO, HO) = \overbrace{(C_{12}H_4Cl)H_2N}^{\text{Chloraniline.}} + 4(KO, CO_2) + 2\,H.$$

$$\overbrace{(C_{16}H_3Cl_2)NO_4}^{\text{Dichlorisatin.}} + 4(KO, HO) = \overbrace{(C_{12}H_3Cl_2)H_2N}^{\text{Dichloraniline.}} + 4(KO, CO_2) + 2\,H.$$

$$\overbrace{(C_{16}H_2Cl_3)NO_4}^{\text{Trichlorisatin.}} + 4(KO, HO) = \overbrace{(C_{12}H_2Cl_3)H_2N}^{\text{Trichloraniline.}} + 4(KO, CO_2) + 2\,H.$$

It is particularly to be remarked that the basic properties of the aniline are preserved in these compounds, though with gradually decreasing distinctness; and it is not until the third equivalent of chlorine has been introduced that the basic power finally disappears: thus aniline is powerfully basic; chloraniline is distinctly basic; dichloraniline, feebly so; and trichloraniline is neutral.

Not one of these bodies when in solution, combined with nitric or sulphuric acid for instance, gives any precipitate of chloride when mixed with nitrate of silver; yet a single equivalent of chlorine, in the form of hydrochloric acid, will neutralize the basic power of any of these compounds: thus if hydrochloric acid be combined with aniline so as to form hydrochlorate of this base ($C_{12}H_7N, HCl$), the solution will have all the characters of a neutral salt, and will occasion an immediate precipitate when mixed with nitrate of silver;

$$\overbrace{C_{12}H_7N, HCl}^{\text{Hydrochlor. of Aniline.}} + \overbrace{AgO, NO_5}^{\text{Nitrate of Silver.}} = \overbrace{AgCl}^{\text{Chloride of Silver.}} + \overbrace{(C_{12}H_7N, HO, NO_5)}^{\text{Nitrate of Aniline.}}$$

These differences may be accounted for by the supposition that in the different chlorinated anilines the chlorine has entered more intimately into the composition of the body than in the case just cited, as it is supposed that part of the hydrogen in the molecule of the base has been actually displaced by chlorine in the first cases; whereas, in the last, the chlorine has merely attached itself to the base. The full importance of such processes of substitution will be made manifest as the reader proceeds: and in order to facilitate the acquirement of distinct notions upon this point, we pass next to the consideration of the principal modes in which the chemist effects the metamorphoses of the compounds which come before him.

(918) *Production of Chemical Metamorphoses.*—Three principal methods are employed in examining the chemical composition of organic bodies, and in tracing their relations to other compounds. These three methods are—1. That of *oxidation*. 2. That of *reduction*. 3. That of *substitution*, including double decomposition.

1. *Oxidation*—It will be unnecessary to consider minutely the effects of rapid direct oxidation or combustion, as the general result in all cases where a sufficient amount of air is supplied is to convert the carbon into carbonic acid, and the hydrogen into water, whilst the nitrogen is commonly liberated in the free state. It is the study of the process of gradual oxidation which affords results so instructive to the chemist. When an organic body is placed in contact with a powerful oxidizing agent, such as nitric acid, chromic acid, or a mixture of sulphuric acid and black oxide of manganese, the effects which are produced will vary in different cases. In some compounds hydrogen alone will be oxidized, as when alcohol is submitted to distillation with chromic acid; in which case water is produced, and a new body, aldehyd, containing all the carbon of the alcohol is produced:—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} + O_2 = \overbrace{C_4H_4O_2}^{\text{Aldehyd.}} + 2\,HO$$

In other instances, both the carbon and the hydrogen are partially removed in the form of carbonic acid and water, whilst an organic body of less complex composition is left; as when stearic acid is treated with nitric acid: in this case the products vary with the strength of the acid employed, and with the time during which they are left to act upon each other; so that the following compounds, each successively simpler in composition, might be obtained from stearic acid $C_{36}H_{36}O_4$:—

Capric acid .	$C_{20}H_{20}O_4$	Adipic acid .	$C_{12}H_{10}O_8$
Suberic acid .	$C_{16}H_{14}O_8$	Butyric acid .	$C_8H_8O_4$
Pimelic acid .	$C_{14}H_{12}O_8$	Succinic acid .	$C_8H_4O_8$
Œnanthylic acid	$C_{14}H_{14}O_4$	&c.	

But it is not only to the processes of oxidation effected in the laboratory that it is necessary to attend. Oxidizing actions are in constant operation unperceived on every side of us. The gradual decay of organic compounds is owing to their spontaneous slow oxidation: for decay is, in reality, only a slow process of combustion; a fact which Liebig indicates by substituting the term *eremacausis* for that of decay. The decay of wood is a familiar instance of this kind; the hydrogen of the wood becomes more rapidly oxidized than its carbon, and the result is the formation of a brown powder termed ulmin or humus, in which the carbon preponderates over the hydrogen and the oxygen to a much greater extent than in the wood from which it was formed. These slow processes of combustion are intimately connected with the development of ozone, or chemically active oxygen (288). In certain cases the formation of ozone is so abundant during such actions, as to furnish some of the best means of obtaining this singular body. Thus ozone is always formed during the slow oxidation of phosphorus in air; and it appears also to be produced in the oxidation of oil of turpentine and ether under particular circumstances, as when a hot platinum wire is suspended in a mixture of the vapour of ether and atmospheric air. The ozone thus developed has in its turn a powerful influence in promoting the oxidation of the organic body, though of course it cannot be supposed that the presence of ozone is essential to the production and development of such oxidations, for they constantly occur where no ozone can be supposed to exist; whilst in other cases the production of ozone appears to be a consequence rather than a cause of the process.

The importance of studying the action of such cases of oxidation must be obvious, when it is borne in mind that it is always by the agency of oxygen upon the various complex substances contained in the animal body that they are gradually resolved into carbonic acid, water, and ammonia; in one or other of which forms they return again to the domain of inorganic chemistry.

2. *Reduction.*—Processes of reduction are less completely under the control of the chemist than those of oxidation, and they are consequently not applied in the laboratory so easily or so frequently. In a few cases one or two equivalents of hydrogen may be combined with the original compound; thus alloxan, under the influence of sulphuretted hydrogen, furnishes alloxantin:—

$$\overbrace{C_8H_4N_2O_{10}}^{\text{Alloxan.}} + HS = \overbrace{C_8H_5N_2O_{10}}^{\text{Alloxantin.}} + S.$$

and in a somewhat similar manner blue indigo, under the combined action of protoxide of iron and alkalies becomes converted into white indigo :—

$$\overbrace{C_{16}H_5NO_2}^{\text{Blue Indigo.}} + HO + 2\ FeO = \overbrace{C_{16}H_6NO_2}^{\text{White Indigo.}} + Fe_2O_3.$$

Sometimes deoxidation occurs during the process of fermentation; as when malate of lime is allowed to ferment in contact with decayed cheese; succinic, acetic, and carbonic acids being the result: the formula of malic acid differing from that of succinic acid by containing 2 equivalents more of oxygen :—

$$\begin{aligned}&\text{Malic acid}\ \ . = 2\ HO,\ C_8H_4O_8\\&\text{Succinic acid} = 2\ HO,\ C_8H_4O_6.\end{aligned}$$

3. *Substitution.*—The formation of compounds by displacement or substitution, is one of the most important methods of research at the disposal of the chemist. The ordinary method of preparing insoluble inorganic compounds by double decomposition, is simply a case of the substitution of one base or acid for another: when solutions such as those of carbonate of potash and nitrate of baryta are mingled, the barium is exchanged for potassium, and reciprocally potassium for barium; $KO, CO_2 + BaO, NO_5 = KO, NO_5 + BaO, CO_2$. This species of substitution is also a familiar operation amongst the compounds of organic chemistry; for the chemist has learned to displace various elementary substances by compound groups, as when by the mutual action of hydrocyanic acid and red oxide of mercury, cyanide of mercury and water are produced; $HCy + HgO = HgCy + HO$: the hydrogen and the mercury, being mutually substituted the one for the other; whilst the group Cy ($= C_2N$), takes the place of the oxygen in the oxide of mercury. Substitutions of groups of greater complication than these are also readily effected, and it is even possible in some instances to produce a true organic compound from inorganic elements (920).

Few instances of substitution are more remarkable than those by which ammonia may be converted into a complex organic base:—when bromide of ethyl, for example, is mixed with a solution of ammonia in alcohol, placed in a sealed tube and heated for a few hours to 212°, a reaction occurs, in consequence of which, as the mixture cools, crystals of hydrobromate of ethylia (C_4H_7N, HBr) are produced; and if this compound be distilled with hydrate of potash, bromide of potassium, water, and a new base, ethylia, (C_4H_7N) will be formed.

Now, since ammonia may be represented as consisting of $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$; ethylia may in like manner be viewed as $= \left.\begin{matrix}C_4H_5\\H\\H\end{matrix}\right\}N$, or as ammonia in which 1 equivalent of hydrogen has been displaced by C_4H_5, or 1 equivalent of ethyl. The substitution will be understood from the following equations:—

$$\overbrace{C_4H_5Br}^{\text{Bromide of Ethyl.}} + H_3N = \overbrace{C_4H_5,\ H_2N,\ HBr}^{\text{Hydrobromate of Ethylia.}};\ \text{and}$$

$$\overbrace{C_4H_5,\ H_2N,\ HBr}^{\text{Hydrobromate of Ethylia.}} + KO,\ HO = \overbrace{C_4H_5,\ H_2N,}^{\text{Ethylia.}} + KBr + 2\ HO.$$

Again, if bromide of ethyl be heated similarly with this new base, a second equivalent of hydrogen may be displaced, and a hydrobromate of a second more complicated base, diethylia, ($C_8H_{11}N$) will be obtained; and from this hydrobromate the pure base is liberated by distillation with potash. In diethylia two equivalents of hydrogen are displaced by ethyl:—

$$\text{Thus, diethylia, } C_4H_{11}N, = \left\{\begin{matrix}C_4H_5\\C_4H_5\\H\end{matrix}\right\}N;$$

and, again, if bromide of ethyl be made to act upon diethylia, the third equivalent of hydrogen is displaced, and triethylia ($C_{12}H_{15}N$) in combination with hydrobromic acid is produced; and thus a complex ammonia $\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N$, is built up step by step by the successive removal of hydrogen, and the substitution of a corresponding number of equivalents of ethyl. Many cases of the same nature will be exhibited when the artificial formation of organic bases comes under the notice of the reader (1027).

(919) *Substitution of Chlorine and its analogues for Hydrogen.*—Other remarkable species of compounds which are obtained by substitution, are those in which a portion of the hydrogen of the original body is displaced by chlorine. When a current of dry chlorine gas is passed through certain organic liquids containing hydrogen, the chlorine is rapidly absorbed, especially if the action be aided by exposure to light or to the direct rays of the sun; the organic compound undergoes decomposition, abundance of hydrochloric acid escapes, and a new organic body, into the composition of which chlorine enters, is formed. This decomposition is usually very definite in its nature. In the majority of cases the

new product is perfectly analogous to the compound from which it is furnished, and contains the same number of elementary atoms, but a certain number of equivalents of its hydrogen has been displaced by a corresponding number of equivalents of chlorine; so that for every equivalent of hydrogen removed in the form of hydrochloric acid, an equivalent of chlorine has been substituted. This very singular species of substitution was originally observed by Gay Lussac to take place when wax is acted upon by chlorine; and a good example of its occurrence has already been considered, when engaged in tracing the conversion of Dutch liquid into sesquichloride of carbon (400). This kind of substitution is of frequent occurrence, and some of the most instructive instances are afforded by the action of chlorine upon ether and upon other derivatives of alcohol. For example, when the vapour of hydrochloric ether (C_4H_5Cl) is subjected to the action of chlorine in the direct rays of the sun, the chlorine immediately begins to act upon the ether, and the action may then be continued in diffused daylight. The experiment may be conducted in an apparatus similar to that used in preparing Dutch liquid, and shown in fig. 275, part ii. page 630. In order to supply the hydrochloric ether, a mixture of hydrochloric acid and alcohol is placed in the retort *a*, and warm water substituted for sulphuric acid in the bottle *c*. By attention to a number of precautions, a succession of compounds is furnished, in which equivalent for equivalent the hydrogen is displaced by chlorine, until at length the last product obtained is sesquichloride of carbon. The following table exhibits the successive steps of the reaction, and indicates some of the properties of the different compounds:—

		Boiling pt.	Sp. gr.	Dens. vap.
Hydrochloric Ether . .	C_4H_5Cl	52°	0·874	2·219
Chlorinated ditto . . .	$\left.\begin{matrix}C_4H_4Cl\\Cl\end{matrix}\right\}$	147°	1·174	3·478
Dichlorinated ditto . .	$\left.\begin{matrix}C_4H_3Cl\\Cl_2\end{matrix}\right\}$	171°	1·372	4·530
Trichlorinated ditto . .	$\left.\begin{matrix}C_4H_2Cl\\Cl_3\end{matrix}\right\}$	215°	1·530	5·799
Tetrachlorinated ditto .	$\left.\begin{matrix}C_4H\,Cl\\Cl_4\end{matrix}\right\}$	295°	1·644	6·975
Sesquichloride of Carbon	C_4Cl_5Cl	360°	2·4	8·15

The density of these compounds, both in the state of liquid and of vapour, increases as the quantity of chlorine increases; the volume of 1 equivalent of vapour is the same for all, and it occupies a space equal to 4 times that of an equivalent of oxygen. It will also be seen that the boiling point rises as the quantity of chlorine increases. An equivalent of each of these bodies contains the same number of elementary atoms, which appear to be grouped in the same order in each compound. The chlorine appears to have taken the place of hydrogen in the group without disturbing the relative position of the other elements which enter into its formation, just as a brick in an edifice may be conceived to admit of being removed whilst its place is supplied by a block of wood or of stone without altering the form or symmetry of the building.

A striking proof of the persistence of the molecular arrangement of the compound, and of the preservation of the relative collocation of its component particles, is afforded when two parallel series of isomeric substitution compounds are compared with each other. Such a parallel is afforded by the chlorinated compounds derived from hydrochloric ether and from Dutch liquid.

It has already been explained (400), that when equal volumes of gaseous chlorine and olefiant gas are mixed together, they gradually enter into combination, and form the oily fragrant body known as Dutch liquid ($C_4H_4Cl_2$): and further, that when this liquid is submitted to the action of chlorine in excess, a series of compounds is obtained from it, in which each equivalent of hydrogen in succession is displaced by chlorine. Now it will be found, on comparing these bodies with those furnished by acting upon hydrochloric ether, that a certain number of them are metameric in pairs, although the two members of each pair possess very different properties, as may be seen by examining the following table, where the metameric pairs are placed side by side :—

		Boiling Point.	Specific Gravity.	
			Liquid.	Gaseous.
Dutch Liquid	C_4H_3Cl, HCl	184°	1·280	3·478
Monochlorinated Hydrochloric Ether	C_4H_4Cl, Cl	147°	1·174	
Monochlorinated Dutch Liquid	$C_4H_2Cl_2, HCl$	239°	1·422	4·613
Dichlorinated HCl Ether . .	$C_4H_3Cl_2, Cl$	171°	1·372	4·530
Dichlorinated Dutch Liquid .	C_4HCl_3, HCl	275°	1·576	5·767
Trichlorinated HCl Ether. . .	$C_4H_2Cl_3, Cl$	215°	1·530	5·799
Trichlorinated Dutch Liquid .	C_4Cl_4, HCl	307°	1·663	6.975
Tetrachlorinated HCl Ether .	C_4HCl_4, Cl	295°	1·644	
Sesquichloride of Carbon . .	C_4Cl_5, Cl (?)	356°	Solid.	8·157
Sesquichloride of Carbon . .	C_4Cl_4, Cl_2 (?)		2·40	

An equivalent of each of these compounds in the gaseous state occupies four volumes of vapour; consequently the densities of each isomeric pair in this condition nearly coincide; indeed it is a necessary condition, that equal weights of all metameric bodies yield equal volumes of vapour, and therefore, allowing for errors of experiment, metamerides must always coincide in density in the gaseous state: but in the liquid form, the densities of the components of each pair are widely different, and the temperatures at which they boil are also different. There is likewise a marked difference in their chemical properties, and in the mode of their decomposition. The following are some of the points of difference. The substitution compounds derived from hydrochloric ether are scarcely affected even when boiled with an alcoholic solution of potash, or with one of hydrosulphate of potassium (KS, HS); and potassium may remain in them at ordinary temperatures without being acted upon. On the other hand, when the compounds derived from Dutch liquid are treated with an alcoholic solution of potash, they are rapidly decomposed, chloride of potassium and water are formed, and a new substance, considerably more volatile than the original chlorinated compound, is obtained: thus,

Dutch liquid.

$$\overline{C_4H_3Cl, HCl} + KO, HO = C_4H_3Cl + KCl + 2\ HO.$$

By the action of Hydrate of Potash.			New Compounds.	Boiling ° F.	Sp. gr. Liquid.
Dutch liquid . . .	C_4H_3Cl, HCl	yields	C_4H_3Cl	14°	
Monochlorinated ditto	$C_4H_2Cl_2, HCl$	,,	$C_4H_2Cl_2$	95°	1·250
Dichlorinated ditto . .	$C_4H\ Cl_3, HCl$	,,	$C_4H\ Cl_3$		
Trichlorinated ditto .	$C_4\ \ Cl_4, HCl$	,,	$C_4\ \ Cl_4$	251·6°	1·619

If an alcoholic solution of hydrosulphate of potassium be employed instead of the hydrated alkali, various sulphuretted compounds are produced, and the chlorinated derivatives of Dutch liquid are evidently decomposed by potassium.

Thus it is obvious that the original difference of molecular grouping is preserved throughout, both in the series of Dutch liquid and in that of hydrochloric ether, so that the chemist is thus, as it were, enabled to dissect these compounds by the agency of chlorine; and it is not until the last equivalent of hydrogen is removed that the molecular arrangement breaks down; both groups in that case yielding the same compound—viz., the sesquichloride of carbon.

The discovery that the substitution of chlorine for hydrogen was possible, at first excited the greatest astonishment amongst chemists, since owing to the powerful affinities of chlorine, particularly when its electrical opposition to hydrogen is borne in mind, the possibility of such an occurrence was never suspected. The displacement of oxygen by chlorine was familiar to the mind of the chemist, but the displacement of hydrogen by chlorine was a fact in opposition to the doctrines of affinity then prevalent. The discovery of this remarkable fact has led to the production by substitution of an immense number of analogous compounds in other groups of organic bodies. The new products so obtained, however, are in general possessed of but little intrinsic interest. The importance of accurately studying the steps by which these substitutions are effected, can, however, be scarcely overestimated, owing to the light which they frequently throw upon the views of the composition of organic compounds, and of their relations to others where no obvious connexion had been previously traced.

It seldom happens that the process of substitution can be followed through its successive stages so completely as in the case of hydrochloric ether or of Dutch liquid; the products of the operation are mingled with each other, and often cannot be satisfactorily separated. The first equivalents of hydrogen are separated more readily than the others, and frequently the last equivalent is removed with great difficulty. It is often necessary at first to moderate the action by cooling the liquid artificially, and by placing it either in obscurity or only in the diffused light of day; whilst to complete the displacement of the last portions, the strongest sunlight, aided by a temperature of ebullition, is frequently requisite. Substitutions of bromine and iodine for hydrogen may also be effected by analogous methods, although, owing to the feebler affinities of these elements, the reactions take place with less vehemence.

In other instances peroxide of nitrogen may be substituted for hydrogen, as when benzole, $C_{12}H_6$, is acted upon by nitric acid, and is converted into nitro-benzole $\left.\begin{matrix} C_{12}H_5 \\ NO_4 \end{matrix}\right\}$ whilst water is formed. Each equivalent of nitric acid in these cases loses 1 equivalent of oxygen, which combines with an equivalent of hydrogen, whilst an equivalent of peroxide of nitrogen takes the place of the latter: thus,

$$\overbrace{\left.\begin{matrix} C_{12}H_5 \\ H \end{matrix}\right\}}^{\text{Benzole.}} + NO_5 = \overbrace{\left.\begin{matrix} C_{12}H_5 \\ NO_4 \end{matrix}\right\}}^{\text{Nitro-benzole.}} + HO.$$

(920) *Synthetic production of Organic Compounds.*—A combination of the operations of direct chemical action with those of substitution, enables the chemist in some instances to build up a truly organic compound from inorganic materials. This is well exemplified in the artificial production of acetic acid in the manner first pointed out by Dr. Kolbe (Liebig's *Annal.* liv. 186):—When carbon is heated to bright redness in the vapour of sulphur, combination between the two elements takes place, and bisulphide of carbon, CS_2 (or C_2S_4), takes place. When bisulphide of carbon is treated with aqua regia, a white volatile crystalline compound is obtained, which is insoluble in water, but soluble in alcohol and in ether: it melts at 275°, and at 338° it enters into ebullition: it has a peculiar odour which brings tears into the eyes, and its vapour has a sp. gr. of 7·43. This substance has the composition represented by the formula $C_4Cl_8S_4O_8$ $[= 4(CCl_2SO_2)]$, and is termed by Kolbe *sulphite of perchloride of carbon.* When this compound is transmitted in vapour through a tube at a dull red heat, it is decomposed into the liquid protochloride of carbon (C_4Cl_4), sulphurous acid, and free chlorine:—

$$(C_4Cl_8S_4O_8) = C_4Cl_4 + 4\,Cl + 4\,SO_2.$$

Now if the protochloride of carbon be placed beneath a layer of water, and exposed in a large vessel filled with chlorine gas, to the sun's rays, sesquichloride of carbon (C_4Cl_6) is formed abundantly, and at the same time an acid solution is obtained which, after saturation with lime or with some other base, is found to contain a chloride and a chloracetate of the base; if lime be used, the formula of the salt is (CaO, $C_4Cl_3O_3$). The following equation will give an idea of the mode in which this compound might be formed; M. Kolbe attributes its production to the reaction of water upon sesquichloride of carbon at the moment of its formation:—

$$\overbrace{C_4Cl_6}^{\text{Sesquichlor. Carbon,}} \quad + \quad 4\,HO \quad = \quad \overbrace{HO,\ C_4Cl_3O_3}^{\text{Chloracetic Acid.}} \quad + \quad 3\,HCl.$$

Now if chloracetic acid be treated with an excess of potassium in the form of an amalgam, the chlorine is entirely withdrawn from this compound, and its place is supplied by hydrogen; in other words, it is converted into acetic acid:—

$$\overbrace{HO,\ C_4Cl_3O_3}^{\text{Chloracetic Acid.}} + 6\,K + 4\,HO = \overbrace{KO,\ C_4H_3O_3}^{\text{Acetate of Potash.}} + 3\,KCl + 2\,(KO,HO).$$

Thus a complex organic acid is obtained from inorganic mateterials:—the successive steps of the operation being 1. bisulphide of carbon; 2. sulphite of perchloride of carbon; 3. protochloride of carbon; 4. chloracetic acid; and 5. acetic acid.

The earliest and one of the most remarkable instances of the synthetic formation of an organic compound was afforded in the case of urea, which Wöhler discovered might be artificially obtained by the action of cyanic acid on ammonia; for on attempting to evaporate a solution of cyanate of ammonia, this salt undergoes an isomeric transformation, and yields urea:—

$$\overbrace{NH_4O,\ C_2NO}^{\text{Cyanate of Ammonia.}} = \overbrace{N_2H_4C_2O_2}^{\text{Urea.}}.$$

Berthelot has recently succeeded in obtaining formic acid synthetically by combining carbonic oxide with hydrate of potash;

$$C_2O_2 + KO,\ HO = \overbrace{KO,\ C_2HO_3}^{\text{Formiate of Potash.}}.$$

Strecker has likewise succeeded in obtaining taurin by synthesis, and there can be no doubt that as researches in this direction are multiplied, new methods of preparing bodies as yet obtainable only from the products of the living plant or animal, will be devised.

CHAPTER II.

THE SACCHARINE OR AMYLACEOUS GROUP.—VARIETIES OF FERMENTATION.

(921) THE compounds which belong to the group to which the following chapter is devoted, are among the most important and abundant constituents of plants. One of the most remarkable features of their chemical composition is the circumstance that they all contain oxygen and hydrogen exactly in the proportion requisite to form water, and hence they have by some writers been spoken of as *hydrates of carbon*. This term, however, is by no means intended to signify that all the hydrogen and oxygen exist in them united in the form of water, but merely to indicate that the proportion of their components is such as might admit of their elements being so arranged. Owing to this peculiarity of composition, many of these bodies admit of being readily transformed one into the other by the addition or abstraction of the elements of water, and several of them are especially prone to undergo the changes produced by fermentations of various kinds.

When submitted to oxidation by the action of nitric acid, most of them yield oxalic acid; and under the influence of a mixture of concentrated nitric and sulphuric acids, substitution compounds are obtained, in which a portion of their hydrogen is displaced by peroxide of nitrogen. The most remarkable of these substitution compounds is pyroxylin (gun-cotton), the peculiar inflammability and explosive character of which is well known; but all of the nitrous substitution products of this class partake more or less of the inflammable and explosive properties which are so signally exhibited by pyroxylin.

In the present chapter the compounds mentioned in the following table will be described; in a few of the substances enumerated in the lower part of the table, the proportion of oxygen and hydrogen in them differs from that of the sugars and starches.

Amylaceous and saccharine group.

Cane sugar (sucrose)	$C_{12}H_{11}O_{11}$
Fruit sugar (fructose)	$C_{12}H_{12}O_{12}$
Starch sugar (glucose)	$C_{12}H_{12}O_{12}$, 2 Aq
Milk sugar (lactose)	$C_{24}H_{19}O_{19}$, 5 Aq
Melitose	$C_{24}H_{24}O_{24}$, 4 Aq
Eucalyn	$C_{12}H_{12}O_{12}$, 2 Aq
Sorbin	$C_{12}H_{12}O_{12}$
Inosite	$C_{12}H_{12}O_{12}$, 4 Aq
Starch	$C_{12}H_{10}O_{10}$
Dextrin	$C_{12}H_{10}O_{10}$
Inulin	$C_{24}H_{21}O_{21}$
Gum (arabin)	$C_{12}H_{11}O_{11}$
Cellulose	$C_{36}H_{30}O_{30}$
Mannite	$C_6H_7O_6$
Dulcose	$C_{12}H_{14}O_{12}$
Quercite	$C_{12}H_{12}O_{10}$
Pectin	$C_{64}H_{40}O_{56}$, 8 Aq
Glycyrrhizin	$C_{36}H_{22}O_{12}$, 2 Aq

Certain only of these substances are soluble in cold water, viz., the sugars and the gums. Others, like starch, become dissolved in water by the aid of heat, or rather become diffused through the liquid, though the solution is of a very imperfect character; whilst a third variety, cellulose or ligneous fibre, is quite insoluble in water, whether hot or cold.

§ I. THE SUGARS.

(922) FOUR principal varieties of sugar are known to the chemist. The most important of these is the common sugar, furnished by the sugar cane, hence termed *cane sugar.* The second is that to which most acidulous fruits owe their sweetness; it forms a syrupy liquid which does not crystallize, and which is abundant in treacle: it is often termed *fruit sugar.* The third variety is frequently formed from the second; it constitutes the hard granular sweet masses which are common in old dried fruits, such as raisins, figs, &c.: it is known as *grape* or *starch sugar,* the latter name being derived from a method of preparing it artificially by boiling starch with a dilute acid. The fourth variety is that to which milk owes its sweetness: it has never been met with excepting in the milk of animals, and hence it is termed *milk sugar.*

These different varieties of sugar agree in possessing a powerfully sweet taste. Each, when pure, has always a definite degree of sweetness, but there are great differences in the relative sweetness of the different varieties. A pound of cane sugar, for example, will produce a greater sweetening effect than a pound of fruit sugar; and at least two pounds and a half of starch sugar are required to produce a sweetening effect equal to that of one pound of the cane sugar; while a given weight of the sugar from milk possesses less sweetening power than an equal quantity of starch sugar.

These varieties of sugar differ greatly in external appearance as well as in chemical characters; and they also differ in chemical composition. If quantities of the different kinds of sugar which contain equal amounts of carbon be compared together, it will be found that they differ in the proportion in which the elements of water are present. Comparing together quantities of sugar which contain 12 equivalents of carbon, the proportion of water in each variety will be as follows:—

		Carbon.	Water.
Cane Sugar . .	$C_{12}H_{11}O_{11}$	72	99
Fruit Sugar . .	$C_{12}H_{12}O_{12}$	72	108
Starch Sugar . .	$C_{12}H_{12}O_{12}$, 2 aq.	72	126
Milk Sugar . .	$C_{24}H_{24}O_{24}$	72	108
Ditto dried . .	$C_{24}H_{19}O_{19}$	72	85·5

There are few plants from which sugar is absent, and to which, at some period of their growth it does not form an important article of nutriment.

(923) 1. CANE SUGAR or *Sucrose* ($C_{12}H_{11}O_{11}$).—This variety of sugar is chiefly obtained from the sugar cane; but the sugar maple and the beetroot furnish a considerable quantity for the market; it is also contained in carrots and turnips, as well as in the pumpkin, the chestnut, the young shoots of the maize, and in a large number of tropical fruits.

Properties.—Cane sugar has a sp. gr. of 1·6. It is soluble in about one-third of its weight of cold water, producing the thick, viscid liquid known as syrup. It is also somewhat soluble in alcohol, especially when heated with this liquid. By the spontaneous evaporation of its aqueous solution, it is deposited in large four-sided rhomboidal prisms, terminated by dihedral summits: these crystals constitute sugar candy, which is colourless or brown according as the syrup employed is more or less free from colour. Ordinary loaf sugar consists of a congeries of minute transparent crystals, and the dazzling whiteness of the purest specimens is produced by the numerous reflections and refractions which the rays of light experience within the mass, from the numberless crystals of which it is composed. When two pieces of loaf sugar are rubbed together, a pale violet phosphorescent light is emitted.

If a solution of sugar be boiled it becomes sour, gradually becoming less viscid, and irrecoverably losing its property of crystallizing: this change is attended by the assimilation of an additional quantity of the elements of water, and the simultaneous and consequent formation of the uncrystallizable fruit sugar ($C_{12}H_{12}O_{12}$). This prejudicial alteration is effected still more rapidly by the addition to the sugar of one-twentieth of its weight of oxalic, citric, malic, or any of the stronger acids. If the solution be kept boiling for some hours, the change proceeds still further, two additional equivalents of water being assimilated by the fruit sugar, which thus becomes converted into grape sugar ($C_{12}H_{14}O_{14}$); and at the same time a certain quantity of formic acid, and of a brown sparingly soluble substance termed *ulmin*, are produced. Smaller quantities of the acids produce similar effects, but to an extent proportioned to the degree of acidity. It is to prevent these injurious changes that a small amount of lime is always added to the cane juice immediately after its expression from the plant, and before it is heated. The crystallization of sugar is also prevented by the presence of 2 or 3 per cent. of many salts, such as common salt or chloride of calcium; these salts appear to form definite but deliquescent compounds with cane sugar. According to M. Péligot, the compound with chloride of sodium contains ($NaCl, HO, C_{12}H_9O_9 + C_{12}H_{11}O_{11}$).

The uses of sugar as an article of food are well known. Alone, it is insufficient for the support of life; but when mixed with other suitable food it has a fattening tendency, which however is not greater than that of a corresponding weight of starch (Lawes and Gilbert, *Brit. Assoc. Report*, 1854, p. 417). Sugar is largely used as an antiseptic, in syrups and preserves. If dusted abundantly over meat, fruit, or fermentable matters, it prevents the usual process of decay from occurring, provided that the substances to be preserved are at the same time tolerably well excluded from the air.

(924) *Action of Bases on Sugar.*—Sugar has the property of dissolving many metallic oxides when its solution is boiled with them:—for example, freshly precipitated oxide of lead is taken up by it in considerable quantity; and, on cooling, a white powder consisting of $2\ PbO, C_{12}H_{10}O_{10}$, is deposited; this if dried at 212°, loses an equivalent of water, and becomes $2\ PbO, C_{12}H_9O_9$. Lime is also, in like manner, dissolved by syrup to a large extent; the compound ($CaO, C_{12}H_{11}O_{11}$) has a bitterish taste, and is very soluble in cold water. Its solution, however, if tolerably concentrated, becomes opaque when heated, and presents an appearance of coagulation, resembling that of white of egg: it is deposited by boiling, and may even be washed with boiling water, though it is readily redissolved on cooling. An analogous compound may be formed with baryta. The compounds produced with other bases are sparingly soluble in water, but are readily taken up by alkaline liquids. This fact explains an observation that the presence of sugar prevents the precipitation by alkalies, of many metallic oxides from their salts, the oxides of copper and of iron being amongst the number thus retained in solution. Many metallic oxides experience reduction, either partial or complete, when boiled with sugar; if the chromates, for instance, be mingled with a little free acid, and heated with solution of sugar, the chromic acid is reduced to the sesquioxide of chrome, which is dissolved by the excess of acid, whilst the liquid becomes green. Salts of the red oxide of mercury are converted into those of the suboxide, and salts of gold give a precipitate of the reduced metal in fine powder. This reducing action is also possessed, though to a less extent, by other compounds analogous to sugar.

If sugar be mixed with eight times its weight of quick-lime, and distilled in an earthenware retort, it is decomposed, and a mixture of acetone ($C_6H_6O_2$), and *metacetone* (C_6H_5O), are amongst the products of distillation. The latter is an oily liquid, which does not mix with water, but is soluble in alcohol and in ether; by washing the distilled liquid with water, the acetone may, therefore, be removed, whilst the metacetone is left. Metacetone boils at 183° F. (Fremy). When treated with a mixture of bichromate of potash and sulphuric acid it undergoes oxidation, and is converted into propionic acid ($HO, C_6H_5O_3$). If sugar be treated with three times its weight of hydrate of potash, instead of with quick-lime, propionic acid, mixed with formic and acetic acids, is formed, and the three acids enter into combination with the potash.

(925) *Other modes of decomposition of Sugar.*—Concentrated sulphuric acid rapidly chars and destroys cane sugar. If equal volumes of strong syrup and oil of vitriol be mixed, much heat is evolved, the mass froths up and emits carbonic and formic acids, whilst a black carbonaceous residue is left. A similar blackening effect is produced by some of the metallic chlorides; Maumené has proposed to take advantage of this for the purpose of discovering small quantities of sugar when in solution:—Strips of white merino are to be dipped into a solution of bichloride of tin in an equal quantity of water, and dried at 212°: if a drop of any liquid containing sugar be placed on a slip so prepared, and gently heated, a brown or black stain will be formed: this test is also applicable to the sugar of fruits and of starch. Dry chlorine likewise attacks sugar at a temperature of 212°, and produces a similar brown substance, which is only partially soluble in water. Nitric acid, of sp. gr. of 1·25, converts sugar into saccharic acid (934), with evolution of carbonic acid; but if the nitric acid be more concentrated, oxalic acid is formed.

Cane sugar undergoes an important change under the influence of the yeast of beer, which causes it to experience the alcoholic fermentation; it becomes converted first into fruit sugar, and then into carbonic acid and alcohol (955). In contact with putrefying casein and chalk, lactic fermentation is induced in sugar, the product being lactic acid (959); under other circumstances, not as yet thoroughly investigated, sugar undergoes the viscous fermentation, and becomes changed into a mucilaginous substance, and into mannite (935).

(926) *Action of Heat on Sugar.*—At a temperature of about 320° F., sugar undergoes fusion, and on cooling, forms the trans-

parent, amber-coloured solid, sold by the confectioners as *barley sugar*. If long kept in this form it loses its transparency, and gradually becomes crystallized. This change may be retarded, but not altogether prevented, by adding a small proportion of vinegar to the melted sugar. This alteration in structure is strictly analogous to that in virtue of which the tough, transparent variety of sulphur assumes its crystalline state. It has been observed that in both these cases an evolution of heat occurs during the passage of the bodies from the vitreous to the crystalline condition. Another interesting point of resemblance between these two phenomena is presented in the remarkable difference between the melting points both of crystallized and vitreous sulphur, and of crystallized sugar and barley sugar. The latter becomes liquefied between 194° and 212°, while loaf sugar does not melt below 320°.

A solution of cane sugar exerts a right-handed rotation upon a ray of polarized light (120); but sugar which has long been kept in a melted state, when redissolved in water has lost its power of crystallizing, and no longer exerts any rotatory action on the polarized ray. Soubeiran has also observed that when a solution of sugar is long exposed to an elevated temperature, even where air is excluded, it undergoes a molecular change; the liquid becomes brown, and gradually acquires a left-handed rotatory action upon the ray. The simple boiling of cane sugar with water, if long continued, gradually causes the sucrose to combine with the elements of water, and it thus becomes converted into starch sugar. This change is effected much more rapidly in the presence of chloride of ammonium, or of any of the chlorides of the metals of the earths, such as chloride of calcium.

If the application of heat to the melted sugar be continued, and it be gradually raised to 400° or 420°, the sugar loses two equivalents of water, and a brown deliquescent and nearly tasteless mass remains, which is known as *caramel* ($C_{12}H_9O_9$). This body is often used by cooks and confectioners as a colouring matter. Caramel is soluble in water, and is precipitated from its solution as a brown powder, by adding a large excess of alcohol. It differs from sugar in not being susceptible of fermentation. Caramel forms an insoluble compound with baryta; and if its solution be mixed with one of the basic acetate of lead, a precipitate is formed. If sugar or caramel be heated beyond 420°, inflammable gases escape, and the compound is completely decomposed, leaving a porous brilliant mass of charcoal.

(927) 2. FRUIT SUGAR or *Fructose*, ($C_{12}H_{12}O_{12}$), exists ready

formed in most ripe acidulous fruits, which owe their sweetness to this substance. It may also be procured artificially from starch, gum, and ligneous fibre, under the influence of diluted sulphuric acid; these bodies becoming combined with an additional quantity of water, by a change resembling that just described as taking place when cane sugar is similarly treated; by continued boiling of this acid liquid the sugar passes into the third variety, assimilating two additional equivalents of water. When its solution, after the neutralization of the acid by carbonate of baryta, is evaporated, the grape sugar is obtained in the form of crystals. This passage of fruit sugar into grape sugar sometimes takes place spontaneously, as is seen in the gradual crystallization of the sugar in dried fruits. Fruit sugar is also largely contained in honey, which by long keeping undergoes a spontaneous change into a mass composed chiefly of crystalline grains of starch sugar.

(928) 3. GRAPE OR STARCH SUGAR; *Glucose*, ($C_{12}H_{12}O_{12}$ 2 aq).—*Preparation.*—Starch sugar is prepared upon a considerable scale by allowing a mixture of starch, with a sufficient quantity of water to render it liquid, to flow gradually at a temperature of about 130°, into a vat containing water acidulated with one per cent. of sulphuric acid; this liquor is kept constantly at the boiling point, by which means the starch is at once altered so as not to produce a mucilage. The liquid, after all the starch has been added, is maintained in a state of ebullition for about half an hour, at the end of which time the starch is usually completely converted into sugar. The proportion of starch used amounts to one half of the weight of the water employed. The liquid is drawn off, and the acid is neutralized by adding chalk in small quantities at a time, until it ceases to occasion any effervescence; the precipitate is allowed to subside, and the clear solution is concentrated by evaporation until it acquires a density of 1·28. It is drawn off from the deposited sulphate of lime, after which it is set aside for some days to crystallize. The molasses is allowed to drain off, and the sugar is dried at a gentle heat in a current of air (Pelouze and Fremy, *Traité*, 2nd ed., iv. 570).

The formula for starch is $C_{12}H_{10}O_{10}$, and since that of starch sugar is ($C_{12}H_{14}O_{14}$), the conversion of starch into sugar may be regarded in the light of a mere combination of starch with the elements of water.

A similar conversion of ligneous fibre into sugar may be effected under the influence of acids, but in this case the acid is employed in a more concentrated form; 2 parts of clean linen or calico cut into shreds, are added gradually to 3 parts of oil of vitriol, and allowed to stand for 24 hours. The mixture is afterwards diluted largely with water, and boiled for a few hours. The acid may be neutralized by the addition of chalk, or, what is better, of carbonate of baryta, and the sugar can then be separated from the insoluble sulphate of lime, or sulphate of baryta.

Glucose appears to be the form of sugar which is occasionally met with as a morbid constituent of the urine in cases of diabetes. It has been shown by Bernard to be one of the normal constituents of the liver, and the same physiologist has remarked, that by irritating with a needle the fourth ventricle of the brain in a dog or a rabbit, sugar is developed in the blood and in the urine, after a few minutes.

Grape sugar is distinguished from cane sugar by several characters; it is considerably less soluble in water than cane sugar, though it is more readily taken up by alcohol, and crystallizes from a hot solution of alcohol containing not more than 5 per cent. of water, in anhydrous prisms ($C_{12}H_{12}O_{12}$). It requires nearly two parts and a half of glucose to produce the same sweetening effect as is produced by one part of cane sugar. The action of sulphuric acid upon grape sugar is quite different from its effect upon cane sugar, as instead of decomposing it as occurs with sucrose, it forms with glucose a definite compound acid, which has been termed *sulphosaccharic* acid, and which, according to M. Péligot, yields a soluble salt with lime and with baryta.

Glucose crystallizes with difficulty in warty concretions, composed of hard transparent cubes. It forms with common salt a compound that crystallizes with facility, thus furnishing another distinctive character of this variety of saccharine matter.

Grape sugar forms definite but unstable combinations with the alkaline bases. These compounds, even at ordinary temperatures, gradually undergo change; their solution, which is at first strongly alkaline, becomes neutral, owing to the formation of a powerful, colourless, but uncrystallizable acid, *glucic acid* ($3\ HO, C_{12}H_5O_5$; Péligot), which remains in combination with the base. Glucic acid, when boiled with water, absorbs oxygen and becomes brown; a new acid ($2\ HO, C_{18}H_9O_8$), which Mulder terms *apoglucic acid,* is formed: it is not crystallizable. If an alkaline solution of grape sugar be heated, the sugar is rapidly destroyed, and a different body of dark brown colour, also possessed of acid characters, is produced; this substance is not crystallizable; it has been termed *melassic acid.* This body has a powerful affinity for oxygen, and when boiled with an alkaline solution, to which a salt of black oxide of copper has been added, speedily reduces the black oxide of this metal to the condition of the red oxide.

Upon these facts M. Barreswil has founded a simple method of estimating the amount of sugar which any mixture may contain. For this purpose he prepares an alkaline solution of tartrate of copper and potash, of known strength. A given volume of this solution is placed in a porcelain capsule, and heated nearly to its boiling point; the solution of sugar to be tested is then added by degrees from a burette, until the addition of the syrup ceases to produce any further precipitate. The proportion of sugar which is present in the liquid will be inversely as the volume of the saccharine solution consumed. Cane sugar, however, does not reduce the alkaline solution of tartrate of copper, consequently no indication of the presence of cane sugar is afforded by this reagent. Nevertheless, a quantitative determination even of this variety of sugar may be effected by means of this method, provided that a given volume of the saccharine liquid, acidulated slightly with sulphuric acid, be diluted with water, and boiled for two or three hours; the cane sugar is thus converted into fruit sugar, and on diluting this liquid with water till it occupies a definite volume, the proportion of altered sugar which it contains may be ascertained. Supposing both kinds of sugar to be present, a preliminary experiment is made before boiling with acid, in order to estimate the amount of fruit or of grape sugar, and by deducting this from the quantity found after acidulating the liquid and boiling, the proportion of cane sugar is ascertained. Fehling recommends for the preparation of the standard copper solution, the following proportions as reduced to English weights:—1 ounce of crystallized sulphate of copper, 3 ounces of cream of tartar, 1½ ounce of pure carbonate of potash, 14 or 16 ounces of a solution of caustic soda (sp. gr. 1·12), and water, until the solution measures 15160 water grains. 200 measured grains of this solution contain a quantity of copper, which would be reduced by 1 grain of sugar ($C_{12}H_{12}O_{12}$); 1 equivalent of sugar reducing 10 equivalents of the black oxide of copper to the state of suboxide. This test is often conveniently resorted to as a preliminary trial for sugar in urine: little or no action occurs when a solution of grape or diabetic sugar is mixed with an alkaline solution of copper in the cold; but on the application of a gentle heat the yellow hydrated suboxide of copper is thrown down, and on raising the temperature to the boiling point the red anhydrous suboxide is deposited.

When grape sugar is heated, it begins to soften at about 140°, and at 212° it melts and loses two equivalents of water; at 284°, three additional equivalents of water are expelled, and the residue consists of caramel.

(929) *Effects of the Varieties of Sugar on Polarized Light.*—Both sucrose, or cane sugar, and glucose produce rotation upon a ray of polarized light. The plane of polarization is rotated from left to right, by sucrose rather more powerfully than by glucose. It is remarkable that fruit or uncrystallizable sugar produces an opposite rotation, viz., from right to left. Since the degree of rotation is proportionate in columns of equal length to the quantity of sugar present, it has been proposed to employ this property in order to determine the quantity of sugar present in syrups.

M. Clerget, in a paper contained in the *Annales de Chimie,* III. xxvi., 175, gives a detailed account of the application of polarized light to the analysis of saccharine solutions by the aid of an instrument invented by M. Soleil. Dr. Bence Jones has applied the method to the determination of the quantity of sugar which remains in the unfermented state in wines. Diabetic urine may also be examined by the same process. According to M. Clerget, if the right-handed rotating power of a given weight of cane sugar be taken as 100, that of an equal weight of diabetic sugar is 73, the rotation in this case also being right-handed. In connexion with the optical examination of syrups, the following facts are important:—Starch sugar presents three modifications when examined by its effect upon polarized light. A solution of crystallized starch sugar, when freshly made, possesses a rotatory power double of that which it retains after having been kept in solution for some hours; and the rotatory power of a solution of sugar from malt when freshly made, is three times as great as that of the same solution after long keeping. These different varieties may all be immediately reduced to the one possessed of the minimum rotatory power, by simply heating the solution to 180° or upwards, and then allowing it to cool. If the rotatory power of starch sugar, of minimum effect, be taken as one, that of a fresh solution of crystallized starch sugar will be two, that of sugar of malt three, and that of an equivalent quantity of dextrin (937) will be equal to four.

Starch sugar thus reduced to its minimum power of rotation, undergoes no change when heated for a short time with an acid; but the rotatory power from left to right, possessed by a solution of cane sugar, is reversed (*interverti*) by mixing the liquid with one tenth of its bulk of a pure concentrated solution of hydrochloric acid, and heating it by means of a water bath for ten minutes to the temperature of 154° F.: the crystalline sugar is thus converted into the uncrystallizable form. It has been remarked, that the addition of a solution of potash or of soda to a solution of sugar, reduces the rotatory action of the liquid upon the polarized ray, but on neutralizing the alkali the original effect is restored. An excess of acid exerts no sensible effect upon the rotatory power of the liquid. Mitscherlich has shown that elevation of temperature produces a very singular effect upon the rotatory power. In the case of cane sugar, the rotatory power diminishes slowly as the temperature rises. If the rotatory power at 32° be $=1$, it will at 212° be less by 0·0232 (or $= 0{\cdot}9768$ Dubrunfaut); but in the case of fruit sugar the effect is so considerable that not only is its rotatory power to the left greatly reduced, but it at a certain point becomes null, and beyond this it is actually reversed, and becomes right handed.

(930) *Manufacture of Sugar.*—The chief source of sugar in the state in which it is offered for sale is the sugar-cane, of which there are three or four varieties. This plant is a solid, jointed reed, which grows to a height varying from six to fifteen feet. The sugar-cane flourishes best between the tropics, and requires a strong deep soil. It is found most advantageous to cut the canes before they are allowed to flower, the produce of sugar being much reduced after inflorescence. The canes are cut as close to the soil as possible, since the juice contained in the lowest joints is the sweetest. The ripe canes immediately after cutting are stripped of their leaves, and subjected to strong pressure by passing them between grooved iron cylinders. In that hot climate the juice, if left to itself even for half an hour, begins to ferment: it is, therefore, immediately mingled with $\frac{1}{800}$th of its weight of lime, and heated to 140° F. in large flat-bottomed copper pans or clarifiers, which hold from 300 to 400 gallons each. At this temperature the albuminous portions of the juice become coagulated and rise to the surface in the form of scum, whilst the free acid is neutralized by the lime. After allowing it to cool for an hour, the clear liquid is drawn off for concentration by boiling. The fuel used for this purpose generally consists of the crushed canes, the ashes of which, in well-managed plantations, are always returned to the soil, and furnish manure for future crops. When the syrup has acquired sufficient consistence, it is run into shallow wooden coolers, and allowed to rest for twenty-four hours; at the expiration of that

time it is briskly stirred to favour crystallization; the semi-solid mass is then transferred to the curing-house, and is put into the *potting casks*, which are vessels furnished with perforated bottoms to allow the molasses or treacle to drain off. Into each perforation a reed or the stem of a plantain-leaf is placed, extending to the top of the cask, with the view of facilitating the drainage, which requires three weeks for its completion. The crystals are then dried off in the sun, and form the raw sugar of commerce. On an average, one gallon of juice furnishes one pound of sugar. Much waste is, however, incurred in the extraction of the saccharine matter, for according to Dumas 100 parts of fresh cane should yield 90 of juice, and of this 18 or 20 parts are pure sugar. No uncrystallizable sugar is contained in the fresh juice of sound canes, though it occurs in decayed ones. Much of the waste arises from the conversion of the crystallizable sugar into treacle or uncrystallizable syrup, by the high temperature and frequent boilings to which it is subjected. Great improvements have recently been effected in the apparatus for boiling down syrups, by means of which a beautiful crystallized product may be obtained with care from the juice at the first crystallization.

Maple Sugar.—The American Indians manufacture a considerable quantity of sugar from a species of maple (*acer saccharinum*). In order to obtain the juice, they make perforations through the bark, which penetrate from a quarter to half an inch into the wood. Each tree usually has two borings; these perforations are always made upon the side of the tree facing the south, at a height of from sixteen to twenty inches from the surface of the soil. Reeds are placed in each aperture, to convey the juice into suitable vessels. The best season of the year is during the months of March, April, and May, while the sap is rising, from the 22nd of March to the middle of April being the period preferred. Sometimes a second running is taken in the autumn from the same tree, but it is more injurious to the tree than the spring tapping; in autumn the juice does not run for more than four or five days, but it is twice as strong as that which is drawn in spring. A good run gives daily six gallons from each incision, and in an old tree or 'old bush' these six gallons yield one pound of sugar. In a 'new bush,' twelve gallons are required for each pound of sugar: the average quantity of sugar from each tree is about three pounds. If properly treated, the same tree may be tapped for twenty or thirty years in succession. The higher the perforations the sweeter is the juice. Every twenty-four hours the liquid that has collected is concentrated, and the raw crystallized sugar is sold in blocks without further refining.

Beet-root sugar is extracted by pressing out the juice from the ripe roots of the white beet, which are usually gathered in October. The expressed juice contains about 10 per cent. of sugar, which in the fresh juice is entirely of the crystallizable kind; but it is seldom possible to extract in the crystallizable form more than half the quantity which the root contains.

The expressed juice is first mingled with a small quantity of lime, and then boiled; a large portion of the albumen and azotised matters are thus coagulated and rise to the top in the form of a scum, which is carefully removed. The juice is then filtered through a column of animal charcoal; it is concentrated in the vacuum pan and is then filtered a second time through charcoal; it is next evaporated still further, and filtered through coarse cloth bags to remove any suspended particles; after which it is boiled down to the crystallizing point; the syrup at this stage having a sp. gr. of about 1·39.

The crystals of beet-root sugar are longer and flatter than those furnished by sugar from the cane, but they cannot otherwise be distinguished from the latter.

The manufacture of sugar from this root was called into existence by the wars of Napoleon, during which the ordinary supply of the article was cut off from the French. In France, where the principal manufactories of this sugar exist, a good deal of the molasses, which is inferior to that of the cane, is fermented, and furnishes a considerable quantity of spirit of wine, amounting in weight to nearly one-third of the treacle employed; this spirit is purified by distillation; the residuum is evaporated to dryness, and then incinerated for the sake of the alkaline salts which it yields; these salts consist principally of carbonates of soda and potash, with a small proportion of sulphate of potash and of chloride of potassium. Beet-roots contain a large proportion of soluble saline matters, which are by this means economized. The crushed pulp is either employed while fresh as food for cattle, or used as manure for the land.

(931) *Refining of Sugar.*—The process of refining sugar, whether from the cane or the beet-root, is alike for each. Two or three parts of sugar are dissolved in 1 of lime-water mixed with 3 or 4 per cent. of bone black, and the whole is heated in large cisterns by allowing steam to blow up into them through pipes which open into the bottom of the vessel; from these cisterns the syrup

is transferred to a filtering apparatus consisting of tubes of twilled cotton, where it is freed from mechanical impurities, and runs through as a reddish brown syrup. In many establishments this clarification is aided by adding to the syrup a certain quantity of the serum of bullock's blood. The albumen of the serum, on the application of heat, becomes coagulated and rises to the surface, carrying with it entangled in its meshes the greater part of the impurities, which are afterwards removed by skimming.

The reddish syrup which has run through the filters has next to be freed as much as possible from colouring matter, and for this purpose it is a second time filtered; but the filter on this occasion is of a different nature, and consists simply of a bed of animal charcoal, prepared by calcining bones in closed vessels, and subsequently grinding them into a coarse powder. The filters consist of extensive vats twelve or fourteen feet deep, with perforated false bottoms; upon these a layer of ticking is placed, and above this, charcoal to the depth of twelve feet; above this is another layer of ticking covered with a perforated metallic plate. The syrup is allowed to flow evenly over the surface, and by the time it has run through it is colourless.

Owing to the viscidity of the filtered liquid, a high temperature (230° F.) is necessary to make it boil under ordinary circumstances: and at this temperature the sugar quickly passes into the uncrystallizable modification, especially when exposed to the action of the atmosphere. By an ingenious application of the mode in which liquids may be boiled *in vacuo* at a temperature far below their ordinary boiling point (169), this difficulty has been in great measure overcome; and the syrups are now universally boiled down in the *vacuum pan*. In this apparatus the pressure of the atmosphere is removed by means of a powerful air-pump, and a vacuum is maintained above the surface of the liquid in the evaporating vessel, which is a close pan or boiler constructed of a spheroidal form, in order to enable it to resist the pressure of the external atmosphere. The lower half of the pan is double, for the purpose of admitting steam between the coatings; and a spiral steam pipe is also coiled within the boiler, with a view of increasing the extent of heating surface. By this arrangement a supply of steam can be admitted from a neighbouring boiler, the heat being sufficient to cause the syrup to enter in rapid ebullition, whilst all danger of burning the syrup is completely avoided; since the boiling point does not rise above 150° or 160° F. The evaporation is continued until a small quantity of the liquid when placed between the thumb and finger can be drawn out into a thread, which breaks near the thumb and curls back to the finger. When it reaches this point the syrup is emptied into a vessel heated by steam to about 170°; in this *heater* it is strongly agitated with wooden oars until it appears thick and granular. It is upon this agitation in the heater that the whiteness and fineness of the grain in refined sugar depend. Fresh portions of the evaporated liquor are two or three times added to the first, and thus the temperature is alternately raised and suffered to fall. From the heating vats it is transferred into inverted conical moulds, either of sheet iron or of unglazed earthenware; in the apex of each of these is an aperture, which is at first closed by means of a plug. The syrup is again well stirred in these moulds, to favour the escape of air-bubbles, which would otherwise give the mass a honeycombed appearance. After this operation it is left at rest for several hours, at the end of which time, when the plug is removed, the uncrystallized syrup runs into vessels placed below for its reception. The sugar, however, is not yet white; for though the crystals consist of pure sugar, the loaves retain mechanically a large quantity of coloured syrup. In order to get rid of this, a quantity of fine colourless syrup is placed upon the base of each loaf, and this syrup, as it gradually percolates through the porous mass, displaces the impurities. The loaf is finally dried in a stove, and finished for the market by turning it in a lathe.

In many refineries, after the finest quality of sugar has been obtained in the form of loaves in the manner already described, the syrup which drains from them is boiled down again in the vacuum pan, and is obtained in the form of what is termed *crushed sugar*, which is freed from the uncrystallized syrup with great rapidity by an ingenious application of the centrifugal force. The apparatus employed is similar in principle to that which has been long used for drying clothes in laundries. It consists of a cylindrical drum mounted upon a vertical axis, to which a very rapid rotatory movement can be given. The outer wall of this revolving drum is formed of a stout but close metallic network. This drum is enclosed in a second somewhat larger fixed cylindrical vessel in which the liquid portion of the syrup is collected. In order to use the apparatus, a charge of concentrated syrup, which has been allowed to cool, and has thus become converted into a crystalline magma, is transferred to the inner drum of the centrifugal machine. The drum is now put into rapid rotatory motion, the uncrystallized syrup escapes through the pores of the metallic gauze, whilst the crystals are retained upon its inner surface. Between the withdrawal and the introduction of each charge the drum is cleansed by a jet of high-pressure steam, and thus the pores of the metallic network are kept clear.

(932) A singular modification of sugar was observed by Professor Johnston to be furnished by some species of the *Eucalyptus*; it has recently been more accurately examined by Berthelot (*Ann. de Chimie*, III., xlvi. 66) and described by him under the name of melitose.

Melitose ($C_{24}H_{24}O_{24}$, 4 HO) is contained in the manna of the *Eucalyptus*. It is soluble in water, and somewhat soluble in alcohol. Its aqueous solution crystallizes by spontaneous evaporation in slender needles, which have a feebly sweet taste. When heated to 212° it loses 2 equivalents, or 9·2 per cent. of water; if heated to 266° it loses about 1 equivalent more of water, melts, and emits an agreeable odour, whilst it assumes the aspect of barley-sugar. The aqueous solution of melitose produces right-handed rotation of a polarized ray more powerfully than cane sugar. Basic acetate of lead produces a precipitate in its solutions. It does not reduce the salts of copper when boiled with an alkaline solution of these compounds; but if boiled with sulphuric acid, the resulting liquid acquires the power of reducing the salts of copper. When mixed with yeast, melitose experiences the vinous fermentation, but it gives off one half only of the quantity of carbonic acid which glucose would have yielded. Under the influence of yeast it becomes broken up into two portions, one of which undergoes fermentation like fruit sugar, whilst the second portion remains unacted on in the liquid. To the latter body the name of *Eucalyn* has been given. It is a substance of syrupy consistence, and a feebly sweet taste; when dried *in vacuo* at the ordinary temperature, it consists of $C_{12}H_{12}O_{12}$, 2 HO, and at 212° it parts with 2 equivalents of water. It produces right-handed rotation upon a polarized ray. Eucalyn has the properties of sorbin (see table p. 72) in every respect, except that sorbin produces left-handed rotation and is crystallizable. When heated with alkalies it assumes a brown colour, and reduces the salts of copper; at a heat of 392° it becomes converted into a black insoluble mass. Melitose appears therefore to be formed by the union of two varieties of sugar, one of which is fermentable, while the other is not so.

(933) SUGAR OF MILK; *Lactin* or *Lactose* ($C_{24}H_{24}O_{24}$), *Sp. Gr.* 1·543.—This variety of sugar is an animal product, being

obtained solely from the milk of the mammalia. It is produced by the herbivora in greatest abundance, but it is secreted also by the carnivora, although their diet is exclusively of an animal nature.

Preparation.—After the milk has been coagulated the curd is separated, and the whey is concentrated by evaporation until it reaches the crystallizing point. Small pieces of wood are then introduced to act as nuclei upon which the crystals of lactose are deposited. It is thus procured in mammillated masses composed of groups of right four-sided prisms, terminated by four-sided pyramids. The crystals are white and semitransparent; they feel hard and gritty between the teeth, and require 5 or 6 parts of cold water for solution; the liquid thus formed is less sweet to the taste than that produced by an equal weight of starch sugar. Lactose is insoluble in alcohol and in ether. Its aqueous solution produces right-handed rotation of a ray of polarized light. If lactose be heated gradually to 284°, 2 equivalents of water are expelled; but it is remarkable that if the temperature be suddenly raised, the crystals melt, and then lose 5 equivalents of water. When boiled with dilute acids it is very slowly converted into fruit sugar. When pure, this form of sugar is not susceptible of fermentation, but milk itself may be fermented. In this case, under the influence of the casein, the lactose is probably converted into fruit sugar previous to undergoing fermentation. Lactose may be combined with oxide of lead, and forms with it two white insoluble compounds, $C_{24}H_{19}O_{19}$, 5 PbO, and $C_{24}H_{19}O_{19}$, 10 PbO. It also forms compounds with the alkalies and with the alkaline earths, and absorbs both ammoniacal and hydrochloric acid gases. An alkaline solution of lactose when boiled with the salts of copper reduces them, and precipitates the suboxide of the metal. It also reduces the salts of mercury and of silver when heated with their solutions.

(934) *Action of Nitric Acid on the Sugars.*—The action of nitric acid upon the different varieties of sugar is remarkable and characteristic. Sucrose and glucose, when treated with three times their weight of nitric acid, of sp. gr. 1·25 (care being taken that the temperature be not allowed to rise beyond 120° F.), yield a peculiar acid, the *saccharic;* and the same substance may also be obtained from starch, gum, and lignin by similar treatment.

Saccharic Acid (2 HO, $C_{12}H_8O_{14}$).—This acid forms a colourless, inodorous, deliquescent, gummy, uncrystallizable mass, which is freely soluble in alcohol, but sparingly so in ether. It yields two salts with potash; one of which is neutral and very soluble, the other is a sparingly soluble bisaccharate which crystallizes in oblique rhombic needles. This acid is sufficiently powerful to dissolve iron and zinc with extrication of hydrogen. Its neutral salt with baryta is amorphous and sparingly soluble. Saccharic acid has a tendency to form double salts, so that it appears to be dibasic. This acid is isomeric with mucic acid, a very different body produced by the action of nitric acid upon sugar of milk.

If sucrose or glucose be acted upon by nitric acid, of a sp. gr. higher than 1·25, and the temperature be allowed to rise, a large quantity of oxalic acid is formed.

Mucic Acid ($2\,HO, C_{12}H_8O_{14}$).—Sugar of milk, when treated with excess of nitric acid, furnishes *mucic* acid, which is isomeric with the foregoing acid; it may also be produced from gum and mannite by similar treatment. One part of sugar of milk or of gum, when boiled with 4 parts of nitric acid of sp. gr. 1·35 and 1 part of water, on cooling deposits mucic acid in minute, colourless, transparent, tabular crystals, which assume the appearance of a sparingly soluble white gritty powder, insoluble in alcohol. It is a dibasic acid, the salts of which are all insoluble in water with the exception of those of the alkalies: it forms two classes of salts, a neutral and an acid series. The neutral mucate of potash consists of $2\,KO, C_{12}H_8O_{14}, HO$; the bimucate of the same base of $KO, HO, C_{12}H_8O_{14}, HO$. Mucic acid is soluble in concentrated sulphuric acid, with which it forms a crimson solution.

When mucic acid is heated, carbonic acid and water are expelled, and a new monobasic acid, the *pyromucic* ($HO, C_{10}H_3O_5$), is sublimed in delicate needles :—

$$\overbrace{(2\,HO, C_{12}H_8O_{14})}^{\text{Mucic Acid.}} = \overbrace{(HO, C_{10}H_3O_5)}^{\text{Pyromucic Acid.}} + \overbrace{2\,CO_2}^{\text{Carbonic Acid.}} + 6\,HO.$$

Pyromucic acid is isomeric with the pyromeconic and with citraconic acid, but it is distinguished from these bodies by the formation of a white insoluble precipitate when added to a solution of subacetate of lead.

If mucic acid be simply boiled in water for some time, it passes into an isomeric variety known as *paramucic acid*, which is much more soluble in water than mucic acid, and is also freely taken up by alcohol; when its aqueous solution is evaporated, paramucic acid is left in quadrangular tables.

§ II. Other Soluble Substances allied to Sugar.

(935) **Mannite** ($C_6H_7O_6$ or $C_6H_5O_4, 2\,HO$).—This substance

abounds in the drug known as *manna*, which consists of the inspissated saccharine juice of the *fraxinus ornus*, a tree which grows abundantly in Sicily and Calabria. Mannite is also contained in considerable quantity in celery, in onions, asparagus shoots, and in certain kinds of fungi. According to Stenhouse, it is also found largely in many species of sea-weed; the *laminaria saccharina*, when dried, containing as much as 12 or 13 per cent. of it. It is likewise a constituent of the juice which exudes from many varieties of apples and pears; and it is always formed during the viscous fermentation of sugar to which the juice of the beet root is particularly liable; so that it is a substance which, from its extensive distribution, acquires a certain degree of interest.

Mannite may be readily extracted from the manna of the *fraxinus ornus* by digesting it in hot alcohol; as the solution cools the mannite crystallizes in tufts of silky quadrangular prisms. It fuses at 320° without losing weight, forming a colourless liquid, which solidifies on cooling, into a mass of radiated crystals. Mannite is very soluble in water; it has an agreeable sweet taste, and is easily distinguished from cane sugar by the absence of any charring effect when it is treated with sulphuric acid; in fact, the acid combines with it and forms *sulphomannitic acid* ($HO, C_6H_5O_4, 2 SO_3$). Mannite may, as Stenhouse has shown, be distinguished from grape sugar with facility, since it does not become brown when heated with alkaline solutions. It combines with bases; and when its aqueous solution is mixed with one of basic acetate of lead, a precipitate ($C_6H_5O_4, 2 PbO$) is formed, which consists of mannite, in which 2 equivalents of water have been displaced by 2 equivalents of oxide of lead. Solutions of mannite do not reduce the alkaline solution of tartrate of copper when boiled with it, but when heated with a solution of the nitrate of silver they precipitate the metal. They likewise reduce gold from a solution of its chloride.

Mannite is also characteristically distinguished from true sugar, by its insusceptibility of the alcoholic fermentation when mixed with yeast, and by the absence of any rotatory effect upon a ray of polarized light. Nitric acid produces saccharic and oxalic acids when heated with mannite, but no mucic acid. A modification of mannite ($C_6H_6O_5$), to which the name of *pinite* has been given, has been found by Berthelot in the juice of the *Pinus Lambertiana*: it is distinguished by being nearly insoluble in absolute alcohol, and by its power of producing right-handed rotation upon a ray of polarized light.

Glycyrrhizin ($C_{36}H_{23}O_{12}$, 2 HO; Lade).—The sweet principle of the liquorice root is not a true sugar, for it is not susceptible of fermentation. It has a strong tendency to combine with bases, and forms soluble compounds with the alkalies and earths. It is usually obtained by adding an acid to a concentrated decoction of liquorice root, washing the precipitate with cold water, and dissolving it in alcohol; on evaporating this solution, the glycyrrhizin is left in the form of a brilliant, transparent, brownish mass, which is sparingly soluble in cold water, especially if acidulated. It is more soluble in hot water, but its proper solvent is alcohol. The solution has a sweet taste, leaving a disagreeable bitterness upon the palate.

The following table contains a summary of the leading characters of the principal varieties of sugar, including those of a few saccharine substances of less importance—viz., *sorbin, dulcose,* and *quercite,* which it will not be necessary to describe more minutely.

Sugars and some allied Bodies.

VARIETY AND ORIGIN OF SUGAR.	PRINCIPAL PROPERTIES.
Cane Sugar, $C_{12}H_{11}O_{11}$; from sugar cane.	Crystallizes in four or six-sided rhomboidal prisms—very soluble in water, less so in dilute alcohol—specific gravity 1·6—fuses about 320° F.—is not precipitated by subacetate of lead—does not reduce an alkaline solution of tartrate of copper on boiling—produces *right*-handed rotation—undergoes alcoholic fermentation with yeast—combines with alkalies—boiled with dilute acids, yields glucose—with nitric acid, yields saccharic and oxalic acids.
Fruit Sugar, $C_{12}H_{12}O_{12}$; from many recent fruits.	Not crystallizable—soluble in dilute alcohol—not precipitated by subacetate of lead—reduces an alkaline solution of tartrate of copper by boiling—produces *left*-handed rotation—undergoes alcoholic fermentation with yeast—turns brown when treated with alkalies—dilute acids partially convert it into grape sugar by boiling.
Grape Sugar, $C_{12}H_{12}O_{12}$, 2 HO; from dried fruits, or altered starch.	Crystallizes in cubes or square tables—less soluble in water than cane sugar, but more soluble in alcohol—yields a precipitate with ammoniacal acetate of lead—reduces tartrate of potash and copper, and the salts of mercury, silver, and gold when boiled with them—ferments readily with yeast—produces *right*-handed rotation—becomes brown when treated with alkalies—with nitric acid yields saccharic and oxalic acids.
Sugar of Milk, $C_{14}H_{19}O_{19}$·5 HO; from whey of milk.	Crystallizes in four-sided prisms—less soluble in water than grape sugar—nearly insoluble in alcohol and ether—subacetate of lead precipitates its solutions—reduces the salts of copper, silver, and mercury when boiled with them with potash—produces *right*-handed rotation—not directly susceptible of alcoholic fermentation—is converted into glucose by boiling with dilute acids—yields mucic and oxalic acids, with nitric acid.

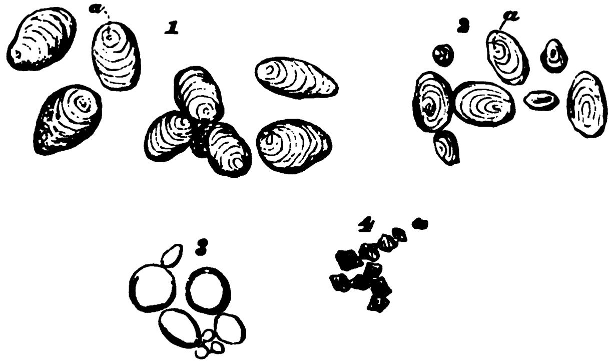
VARIETY AND ORIGIN OF SUGAR.	PRINCIPAL PROPERTIES.
Melitose, $C_{24}H_{24}O_{24}, 4\,HO$; (Berthelot,) from the *Eucalyptus*.	Crystallizes in slender prisms—freely soluble in water, slightly soluble in alcohol—feebly sweet—melts and loses water at 260°—with subacetate of lead yields a precipitate— does not reduce an alkaline solution of tartrate of copper—*right*-handed rotation exceeding that of cane sugar—undergoes alcoholic fermentation with yeast, at the same time half the sugar is separated in an unfermentable form as Eucalyn.
Eucalyn, $C_{12}H_{12}O_{12}, 2\,HO$; (Berthelot,) from fermentation of melitose.	Not crystallizable—precipitates subacetate of lead, and reduces the alkaline tartrate of copper when boiled with it—produces *right*-handed rotation—not susceptible of alcoholic fermentation—becomes brown when treated with alkalies—not altered by boiling with dilute acids.
Sorbin, $C_{12}H_{12}O_{12}$; (Pelouze,) from berries of mountain ash.	Crystallizes in octohedra with a rectangular base—soluble in water, nearly insoluble in alcohol—specific gravity 1·65—fusible without loss of weight—gives a white precipitate with basic ammoniacal acetate of lead—reduces the alkaline solution of tartrate of copper on heating it with it—occasions *left*-handed rotation—is not fermentable—turned brown by alkalies—yields a red solution with oil of vitriol—converted into oxalic acid by nitric acid.
Inosite, $C_{12}H_{12}O_{12}, 4\,HO$; (Scherer,) from muscular tissue.	Crystallizes in radiated tufts—soluble in water, insoluble in absolute alcohol and ether—loses water by heat, and fuses at 410°—does not reduce the salts of copper when boiled with them with alkali—is not susceptible of alcoholic fermentation, but with cheese and chalk yields lactic and butyric acids—is not altered by boiling with dilute acids or alkalies—forms a precipitate with basic acetate of lead.
Dulcose, $C_{12}H_{14}O_{12}$; (Laurent,) origin unknown.	Crystallizes in brilliant prisms—soluble in water and alcohol—fuses at 356° F.—gives no precipitate with subacetate of lead—and does not reduce nitrate of silver or chloride of gold—produces no rotation on polarized light—is not susceptible of fermentation—not affected by dilute alkalies—converted into mucic acid by nitric acid.
Mannite, $C_6H_7O_6$; from the juice of *Fraxinus Ornus*.	Crystallizes in silky anhydrous four sided prisms—soluble in water and alcohol—fusible at 320°—gives a precipitate with basic acetate of lead—by heat reduces the salts of silver or gold—does not reduce the alkaline tartrate of copper when boiled with it—no rotation of polarized light—not fermentable—with nitric acid yields saccharic and oxalic acids—soluble in oil of vitriol, and in alkaline solutions without coloration.
Quercite, $C_{12}H_{12}O_{10}$; from acorns.	Transparent prisms—soluble in water and dilute alcohol—fusible at 420°—does not reduce the alkaline tartrate of potash—not fermentable—soluble without change of colour in oil of vitriol and in the alkalies—yields oxalic acid with nitric acid.

§ III. VARIETIES OF STARCH AND GUM.

(936) STARCH ($C_{12}H_{10}O_{10}$).—The term *starch*, or *amylaceous matter*, or *fecula*, is applied to an organized substance which occurs in rounded or oval grains in the cellular tissue of certain parts of plants. It is met with in great abundance in all dicotyledonous seeds, particularly in those of leguminous plants, such as

peas and beans. The monocotyledonous seeds of the cerealia or corn tribe contain it still more largely; it is also abundant in the tubers of the potato, in the roots of the tapioca and arrow-root, and in a variety of other plants. On examining the grains of starch with a magnifying power of 300 or 400 diameters, they are seen to consist of flattened ovate granules, which in the same plant are tolerably uniform in size, but which vary in magnitude in different species of plants, those of the *canna*, or *tous les mois*, No. 1, fig. 331, being about $\frac{1}{280}$th of an inch in diameter; those of the potato are somewhat smaller, but the grains become larger as the age of the plant increases; those of the arrow-root, No. 2, do not exceed $\frac{1}{800}$th of an inch; those of wheat starch, No. 3, are more circular, and about $\frac{1}{1000}$th of an inch in diameter, and do not exhibit rings; those of rice, No. 4, are angular and often adherent to each other; they do not usually exceed the $\frac{1}{3000}$th of an inch, whilst those contained in the cells of the beet-root are still smaller.

FIG. 331.



Each of the larger grains exhibits a series of concentric rings; some observers consider this appearance to indicate that they have been formed by a deposition of successive layers of starchy matter within an external envelope; Mr. Busk considers that the rings are occasioned by a plication of the envelope itself; in many instances the *hilum*, or supposed point of attachment of the grain to the cellular tissue of the plant from which it was developed, is distinctly perceptible, as shown at *a a*, fig. 331.

The structure of the grains of starch is very beautifully displayed by placing some of them in contact with a drop of concentrated solution of chloride of zinc (tinged with a little free iodine), on the field of the microscope. No change takes place in the granules until a little water is added. They then become of a deep blue colour, and gradually expand; at first a frill-like plicated margin is developed around the globule; by degrees this opens out; the plications upon the globule may then be seen slowly unfolding, and may be traced in many cases into the rugæ of the frill; ultimately the granules swell up to twenty or thirty times their original bulk, and present the appearance of a flaccid sac. During these changes no extrusion of anything within the granules is observed to take place (Busk, *Quarterly Journal of the Microscopical Society*, vol. i.).

The grains of potato starch, if illuminated by polarized light, with a Nicol's prism interposed between the object and the eye, present a well-marked black cross (the centre of which corresponds with the hilum). When wheat starch is subjected to a similar test, this cross is not perceptible; its presence may therefore be of service as a means of distinguishing the fraudulent addition of potato starch or flour to wheat flour.

Properties.—To the unaided eye, starch exhibits the appearance of a white glistening powder, or of columnar masses which are easily reduced to powder; when pressed between the fingers it emits a peculiar sound, and produces a certain feeling of elasticity. Starch is heavier than water. It is insoluble in cold water, alcohol, and ether. If placed in a solution of soda or of potash, which contains two per cent. or upwards of alkali, the granules of starch swell up and become converted into a tenacious paste. A mixture of starch and water may be preserved without change at ordinary temperatures for an indefinite period; but it undergoes a remarkable change when heated to a temperature a little above 140° F. Under these circumstances the exterior layer of the granules absorbs water, the grains swell up, and the mixture suddenly assumes a viscous pasty condition, in which form it is extensively employed by laundresses for stiffening linen. If this paste be largely diluted with water, the swollen granules of the starch slowly subside, whilst a certain quantity of amylaceous matter remains in solution. The starch paste thus obtained does not, when evaporated, recover its former insolubility. Its solutions are precipitated by alcohol, and the precipitate may be redissolved by the immediate addition of water; but after a few hours the flocculi become more coherent and are no longer soluble. A solution of starch produces right-handed rotation of a polarized ray.

It is remarkable, that if starch be boiled under pressure, at about 300° F., with from 5 to 15 times its weight of water, a thin solution is obtained, which may be filtered from the insoluble portion; this liquid, as it cools, deposits minute spherical granules, which, when dried, have the whiteness of starch without its glistening appearance. These granules are sparingly soluble in cold water, but are readily dissolved when the water is raised to 158° or upwards. Iodine tinges them blue, and alcohol causes a precipitate when added to their aqueous solution.

When dry starch is heated sufficiently, it acquires the property of dissolving in cold water, and forms a ropy solution much resembling gum in properties. The grains of anhydrous starch may be heated to 320° F. without becoming soluble, but at 400° the change is complete in the course of an hour or two. Commercial starch, on the contrary, from the water which it retains, is rendered completely soluble by raising the temperature suddenly to 320°, and maintaining it at this point for some time. The change produced in these cases consists in the formation of a substance isomeric with starch, which is termed dextrin. This soluble torrefied starch is known under the name of *British gum,* and constitutes the *leiogomme* of the French manufacturers; it is largely employed by calico printers for mixing with their colours, in order to give them the requisite consistence.

Like most organized structures, starch appears to retain as an essential component, a small quantity of saline matter, consisting partly of potash; and it likewise contains a perceptible amount of some azotised compound, which is contained chiefly in the tegument of the grains (Jacquelain).

A solution of tannic acid occasions a precipitate in one of starch. When a dilute solution of starch is mixed with one of the ammoniacal acetate of lead, an insoluble compound with oxide of lead ($C_{12}H_9O_9 + 2\ PbO$) is formed. Starch may be recognised when present, by the deep blue colour which it acquires on the addition of free iodine to its solution; this colour disappears if the iodine be in excess, or if the solution be heated, but in the latter case it reappears as the liquid cools. If boiled with dilute sulphuric acid, starch quickly loses its viscidity, and is ultimately converted into glucose. Before the transformation is complete, it passes through the same modification that exists in British gum, which has received the name of dextrin, from its property of causing the rotation of a polarized ray from left to right.

Preparation.—In the extraction of starch from the vegetables in which it is contained, advantage is taken of its insolubility in cold water.

1. *Potato Starch.*—This variety is prepared on a large scale from potatoes, which contain about 20 per cent. of amylaceous matter; the cellular tissue of the tuber does not exceed 2 per cent. of the mass, whilst of the remainder, about 76 per cent. consists of water, and the rest of small quantities of sugar, salts, and azotised matters.* In order to extract the starch, the tubers are first freed from adhering earth by a thorough washing, and are then rasped by machinery. The pulp thus obtained is received upon a sieve, and is washed continuously by a gentle stream of water, as long as the washings run through milky. This milkiness is due to the granules of starch which are held in suspension. The milky liquid is received into vats, in which the amylaceous matter is allowed to subside; the supernatant water is drawn off, and the deposit is repeatedly washed with fresh water until the washings are no longer coloured. The starch is then suspended in a small portion of water, run through a fine sieve to keep back any portions of sand, and after having been again allowed to settle, is drained in baskets lined with ticking, and the mass is placed upon a porous floor of half-baked tiles, and dried in a current of air, which is at first of the natural temperature; the drying is completed by the application of a moderate artificial heat.

2. *Wheat Starch.*—A finer species of starch is obtained from the grains of the cerealia, in the preparation of which wheat is largely employed. In making wheat starch a more complicated process is necessary, as in this grain the starch which amounts to nearly 60 per cent. of the whole, is accompanied with an azotised material termed gluten (957), amounting to from 14 to 19 per cent. of the weight of the grain, which also contains a certain quantity of cellular tissue and of sugar. The grain is first coarsely ground and wetted with water. After the lapse of three or four days it begins to ferment, and is then transferred to a large vat

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* The following, according to Boussingault, is the average composition of the tubers of the potato:—

	Moist.	Dry.
Water	75·9	
Albumen	2·3	9·6
Oily matter	0·2	0·8
Fibre	0·4	1·7
Starch	20·2	83·8
Salts	1·0	4·1
	100·0	100·0

where it is mixed with an additional quantity of water, and the fermentation is allowed to proceed for three or four weeks. During this operation the gluten undergoes putrefaction, the sugar and part of the starch become converted into alcohol, and carbonic acid is evolved, while the fermenting mass emits a powerful putrescent odour. A portion of the alcohol and of the starch become converted into acetic and lactic acids, which dissolve that portion of the gluten that has escaped putrefaction, and thus the starch is separated from the materials by which it was accompanied in the grain. It is then repeatedly washed, drained, and dried, as before. The blocks into which it is divided in order to facilitate the desiccation, shrink during the drying into columnar fragments, which are readily pulverized by gentle pressure.

3. *Rice Starch.*—In the foregoing method of preparing starch from wheat, much of the amylaceous matter is wasted, the whole of the gluten is lost, and the operation is attended with the continual evolution of gases of an offensive odour, which are the source of annoyance to the neighbourhood in which the manufacture is carried on. These inconveniences were overcome by Mr. O. Jones, who, in the year 1840, took out a patent for the manufacture of starch, by a method which he applied particularly to rice, though it may be used with other cereal grains. Undried rice contains about 83 per cent. of starch, and about 7·0 per cent. of gluten. The process of Mr. Jones consists in separating these two materials by means of a very weak solution of alkali, which dissolves the gluten, but leaves the starch granules unaltered:—100lb. of rice in the form of grain are macerated in 50 gallons of a solution containing $\frac{1}{360}$th of its weight of caustic soda; after the lapse of 24 hours the alkaline liquid is drawn off, and the rice, after being well washed, is allowed to drain, and is ground into flour. It is then digested for 24 hours longer, in a fresh quantity of ley, with frequent agitation; at the end of that time it is left at rest for 70 hours. The liquid which floats above the starch is then drawn off; it is turbid, has a yellow colour, and contains the gluten of the grain in solution. From this liquid the gluten, which possesses highly nutritive qualities, is recovered by carefully neutralizing the solution with sulphuric acid: it then subsides in flocculi, which are washed, dried, ground into flour, and used for mixing with ordinary flour to increase its nutritive properties.

The deposited starch retains the fibrous matter of the grain; but as this portion is heavier than the fine grains of starch, it is easily freed from the latter, by stirring up the whole with water, allowing the mixture to rest for an hour, during which time the vegetable fibre subsides, and then running off the milky liquid into a separate vessel, where the starch is deposited; after which it is washed, drained, and dried in the usual manner. Starch, in the form in which it is usually sold, retains about 18 per cent. of water. In order to render it anhydrous, it should be dried *in vacuo*, at a temperature of 260° F.

Other sources of Starch.—If during the preparation of starch the temperature employed in its desiccation be raised to 140°, a transparent jelly is produced which, when dry, is no longer farinaceous, but assumes the form of semitransparent granules. *Sago* is the fecula obtained from the pith of the sago palm by making it into a paste with water, and pressing the mixture through a perforated metallic plate; the little cylinders thus obtained are granulated by placing them in a revolving vessel; these are then exposed upon a sieve to a jet of steam, and subsequently dried. *Tapioca* is the starch of the *Jatropha manihot*, which is pressed through a colander, and dried upon a metal plate heated to 212°. It is thus formed into granular, semitransparent, irregular masses. *Arrow root* is the starch of the root of the *maranta arundinacea*, and of one or two other tropical plants. *Salep* is the name given to that yielded by the *orchis mascula*.

The occurrence of starch is not confined to the vegetable kingdom. Granules of starch have recently been found in the brain, and in certain cases of scrofulous caries the liver assumes the peculiar hard, semitransparent, waxy appearance, described by Dr. G. Budd. This condition Virchow has shown to arise from the deposition of amyloid matter in the gland; and a similar deposit has been found in the kidney in the same cases. The deposition of small quantities of starch in the animal tissues, even in health, is not uncommon.

(937) Dextrin ($C_{12}H_{10}O_{10}$) is a transparent, brittle solid, with a vitreous fracture. It is soluble in water and in dilute alcohol, but is insoluble in anhydrous alcohol or in ether; wood spirit dissolves it freely. Dextrin is distinguished by producing right-handed rotation upon a ray of polarized light, and it derives its name from this property. It differs from starch in not yielding any blue coloration with iodine; and from gum by the fact that a solution of dextrin, when mixed with potash, forms a beautiful blue solution on the addition of sulphate of copper, which, on boiling, deposits suboxide of copper; whilst no such effect is produced with gum. Nitric acid converts dextrin into oxalic, not into mucic

acid. M. Payen has contrived a method of preparing dextrin on a large scale, which consists in moistening 10 parts of starch with 3 parts of water containing $\frac{1}{100}$th of its weight of nitric acid, allowing the mixture to dry spontaneously, then spreading the starch upon shelves in layers of an inch and a half in depth, and heating them for an hour or an hour and a half in a stove to about 240° F. When a solution of dextrin is mixed with one of ammoniacal basic acetate of lead, it forms an insoluble precipitate consisting, according to Payen, of $2\ PbO, C_{12}H_{10}O_{10}$.

(938) *Diastase.*—During the germination of seeds the starch undergoes a species of fermentation, and is converted first into dextrin, and subsequently into sugar, in which state it is assimilated by the young shoot. This conversion is due to the action of a peculiar ferment termed *diastase*, which is formed in all germinating seeds. An impure solution of diastase may be readily obtained from malt or freshly-germinated barley by grinding it, moistening it with half its weight of warm water, allowing it to stand, and pressing out the liquid. Malt does not contain more than $\frac{1}{500}$th of its weight of diastase. One part of this substance suffices to convert 2000 parts of starch into dextrin, and subsequently into sugar (Persoz and Payen); the temperature of 150° F. is most favourable to the change, and at 212° this conversion is arrested.

Long before the discovery of diastase, the distillers had found that by mixing a portion of unmalted barley with their malt, and digesting the mixture in warm water for some hours, they obtained an infusion or wort equally sweet with that furnished by an equal weight of malt: 1 part of malt having the power to change into sugar the starch contained in 4 or 5 parts of barley. Now unmalted barley contains but very little sugar, whereas after it has been malted the proportion of sugar is much increased, whilst that of the starch is diminished. Malt is simply barley allowed to germinate up to a certain point, after which its growth is suddenly checked by the application of heat; and it contains a considerable quantity of diastase which has not been expended in the conversion of its starch into sugar. When the mixture of ground malt and barley is digested with water or *mashed*, this excess of diastase acts upon the starch of the unmalted barley, converting it first into dextrin, and subsequently into sugar; a saccharine liquid is thus obtained which is susceptible of fermentation. The preparation of such a sweet wort is the first step in the process of brewing. In malted barley this saccharification of the starch has already taken place during the act of germination, and simple digestion in water extracts the sugar. But since raw barley is less expensive than malt, a certain quantity of it is often substituted for a portion of the germinated grain by the distiller, who sometimes adds as much as 4 parts of unmalted grain to 1 of malt, and thus effects a considerable pecuniary saving.

(939) *Action of Ferments.*—The exact manner in which diastase acts in producing this singular change is unknown, and the same may be said of the mode in which sugar is converted into alcohol and carbonic acid through the intervention of yeast. These actions, however, exhibit considerable analogy with each other, and are connected in some way with the decomposition of the matter serving as a ferment. Moist yeast and moist diastase both very rapidly undergo decomposition. Diastase, when in a state of decay, however, produces changes on other matter entirely distinct from the transformation of starch into dextrin, and an examination of these changes has thrown considerable light on the obscure subject of ferments in general.

It has already been stated that if dextrin be acted on for some time by diastase, it is wholly converted into fruit sugar, but in a certain stage of its decomposition diastase may give rise to products of a different kind; it occasionally converts the dextrin into gum instead of into sugar; at other times mannite is formed; whilst in other cases the starch is converted first into sugar, and this compound is then rapidly transformed into lactic acid. These observations appear to indicate that the same body during its different states of decay may give rise to the formation of products quite different in properties from each other, though all these products, except mannite, have the same ultimate composition. Hence it has been concluded, that the formation of each of these compounds corresponds to a particular phase of decay in the ferment; and it has been supposed that the molecular constitution of all bodies in contact with a ferment, provided that they be susceptible of change, undergoes alterations definite in their nature, and dependent upon the peculiar mode of decomposition which the ferment is itself experiencing. If this explanation be admitted, it is easy to see why in many instances the products of fermentation are of a more or less mixed nature, according as the ferment itself has passed through more or fewer phases of its decomposition.

(940) *Preparation of Malt.*—Upon the proper management of the process of malting much of the success of the subsequent brewing depends. The seasons most favourable for malting are spring and autumn, when the temperature is neither very high nor very low. The barley first undergoes the operation of steeping.

This is effected in stone troughs, where the grain is covered with water to a depth of about six inches. The lighter and decayed seeds float, and are skimmed off, whilst the sound grain, being heavier than the water, subsides. The steeping is continued until the grain becomes uniformly soft, and this occupies generally from forty to sixty hours, the water being changed twice or thrice. During this stage, the barley swells considerably from the moisture which it imbibes, and increases in weight nearly one-half. After a final washing it is drained and then *couched*, or placed in heaps of about fifteen inches in height upon the floor. In these heaps it becomes warm, and continues to swell for the next twenty-four hours: by this time it begins to sprout; as soon as the first whitish protuberance shows itself, the heaps are evenly distributed over the floor of a darkened apartment, and the process termed *sweating* follows. In this state it is allowed to remain several days, usually fourteen; the workmen turning it twice or thrice daily with wooden shovels. This step is employed for the purpose of equalizing the heat, in order that the process of germination may proceed at all points with equal rapidity. By this manipulation the temperature is maintained at a point varying between 55° and 62°. In from ten to twenty days, according to the heat of the weather, the germination is complete; and as soon as the radicle or *acrospire*, as the maltster calls it, has shot to the length of about half an inch, when it bifurcates, and just as the plumula or leaf-shoot is about to make its appearance, the vitality of the seed is extinguished by rapidly drying the grain. In order to effect this object, the malt is spread, to the depth of about two inches and a half, upon floors made of perforated metallic plates. Here it is left to dry in a current of air for some hours, at a temperature not exceeding 90°; at the end of this time a fire is lighted underneath. It is necessary that the greater part of the moisture be expelled before the fire be kindled: afterwards the heat is allowed to rise gradually, but not to exceed 140°, otherwise the starch of the grain would be acted on, and much of the diastase would lose its efficacy. High dried malt is subjected to a much higher temperature, and is actually scorched on the outside. Such malt, however, is used only in small quantity as a colouring ingredient, to give the customary deep brown tinge to *porter*. During the drying, which occupies two or three days, the grain requires frequent stirring, in order that the desiccation may take place regularly. Barley generally yields about 80 per cent. of malt after drying and sifting from the radicles. According to Dr. Thomson, 12 per cent. of this loss is due to water; only 8 per cent. being actually wasted in the form of carbonic acid and trimmings. During the germination, oxygen is absorbed, and a large quantity of carbonic acid is set at liberty. Other grains, such as wheat, oats, rye, and even Indian corn, may be malted, but experience has shown that barley is the grain best adapted to this process. It yields the largest quantity of diastase, although this does not exceed $\frac{1}{500}$th of the weight of the grain. The diastase appears to be developed at the expense of the azotised constituents of the grain. It is generated chiefly in the neighbourhood of the young germ, not of the rootlet.

According to the experiments of Mr. Lawes, of Rothamsted, 100 parts of dry barley yield 90·22 of malt, and 3·99 of malt and kiln dust. It is remarkable that the malt dust, consisting chiefly of the radicles of the seed, carries off with it a great deal of the nitrogen of the grain, amounting to nearly one-ninth of the entire quantity contained in the barley. The loss in nitrogen which barley suffers in becoming converted into malt rises to as much as 13·5 per cent. of the total quantity of nitrogen contained in 100 parts of dry barley. Mr. Lawes found the nitrogen in the barley to amount to 1·78 per cent. of the weight of the dry grain; that contained in dry malt being 1·70 per cent.

(941) *Inulin* ($C_{24}H_{21}O_{21}$; Parnell).—The roots of many plants, among which are those of the dahlia, elecampane (*inula helenium*), colchicum, dandelion, and chicory, contain a variety of starch, to which the name of *inulin* has been given. It is a white, pulverulent, inodorous, tasteless powder, insoluble in alcohol, sparingly soluble in cold water, but readily so in boiling water, from which it is deposited again on cooling in a pulverulent form. Its solution produces left-handed rotation upon a ray of polarized light. By long boiling it assumes the characters of gum. If heated beyond 212° it melts, gives off water, and leaves a scaly, sweetish, gummy mass, which is readily soluble in water. Iodine turns inulin yellow. By boiling with dilute acids it is converted first into dextrin, and then into grape sugar. If heated with nitric acid in the concentrated form, it is converted into oxalic acid. It forms an insoluble precipitate when its solution is mixed with one of acetate of lead and ammonia is added. Mr. Parnell obtained two different compounds in this manner, which when dried at 212° contained, $C_{24}H_{18}O_{18}$, 3 PbO, and $C_{24}H_{21}O_{21}$, 5 PbO.

(942) GUM is found in the juices of almost all plants, but is met with in its purest form in transparent tears, which exude from various species of acacia. Gum arabic may be taken as its type. This variety of gum is frequently described under the name of *Arabin* ($C_{12}H_{11}O_{11}$). It is soluble in water, forming a tasteless, ropy, mucilaginous liquid, which from its adhesive quality often forms a useful substitute for paste or glue. A solution of gum arabic produces left-handed rotation of a polarized ray. It is not susceptible of the alcoholic fermentation. A solution of arabin is precipitated by alcohol and by ether in white flocculi, or if dilute, in the form of a milky turbidity. If boiled with dilute sulphuric acid, it is gradually converted first into dextrin, and then into grape sugar; concentrated nitric acid converts it into mucic and oxalic acids, showing its relation to sugar of milk in this respect: iodine does not alter its colour. It forms soluble compounds with the alkalies and alkaline earths; a solution of gum when mixed with one of subacetate of lead produces a curdy precipitate ($PbO, C_{12}H_{11}O_{11}$). Many other metallic salts, such as persulphate of iron and nitrate of mercury, also precipitate its solution. *Mucilage* or *bassorin* is a modification of gum which is insoluble in water; but, when moistened with this liquid it swells up into a gelatinous mass. It is abundantly contained in gum tragacanth, and accompanies the gum which exudes from the cherry tree. Many seeds, such as linseed, quince-seed, and certain roots, such as those of the marsh-mallow, contain it in large quantity: alkalies render it soluble in water, and appear to convert it into true gum; long boiling in water has a similar effect. Bassorin is precipitated by alcohol, sub-nitrate of mercury, proto-chloride of tin, and sub-acetate of lead. Nitric acid converts it into mucic and oxalic acids.

(943) VEGETABLE JELLY (formerly called *pectin*).—Another principle which, like starch and gum, extensively pervades the vegetable kingdom, is that peculiar body which gives to the juice of many succulent fruits and roots the faculty of gelatinizing. Braconnot first called attention to this substance under the name of *pectin;* it has since been particularly studied by Mulder and by Chodnew; and by Fremy, especially in relation to the ripening of fruits. (*Ann. de Chimie,* III., xxiv. 5.)

According to the last-mentioned chemist, the cellular tissue of many fruits, and of turnips, carrots, parsnips, &c., contains a substance which he terms *pectose*, and which is quite insoluble in water, alcohol, and ether. It possesses the characteristic property of becoming converted, under the influence of dilute acids, aided by a gentle heat, into pectin.

Pectin may be obtained from the juice of ripe pears or apples by throwing down the lime which they contain by the cautious addition of oxalic acid, and then adding a concentrated solution of tannin so long as it occasions a precipitate; the albumen is thus coagulated, and may be separated by filtration. On adding alcohol to the clear liquid, the pectin is thrown down in the form of gelatinous strings. If this precipitate be redissolved in cold water, and again precipitated by alcohol, it may be obtained tolerably pure: when dry it forms a friable mass, which is soluble in water, but insoluble in alcohol and in ether. Its aqueous solution is somewhat viscous: it gives a gelatinous precipitate when mixed with basic acetate of lead, but none with the neutral acetate of this metal. Pectin exerts no action on polarized light. When boiled with water it loses its viscosity, and becomes converted into a modification (*parapectin*), which occasions a precipitate in a solution of neutral acetate of lead. If boiled with dilute acids, an isomeric substance (*metapectin*) is formed, which occasions a precipitate when mixed with a solution of chloride of barium.

Pectic acid ($2\,HO, C_{32}H_{20}O_{28}$; Fremy).—All the above modifications of pectin are rapidly converted into pectic acid by being treated with a solution of a caustic alkali, or of an alkaline carbonate, care being taken to avoid any excess of the alkali. Pectic acid is characterized by its gelatinous nature, whence, indeed, it derives its name (from πηκτὶς, a jelly). It forms soluble compounds with the alkalies, but they do not crystallize; the other pectates are insoluble. Pectic acid is likewise soluble in many of the salts of the alkalies. It is most easily obtained by boiling the washed pulp of carrots or turnips in a weak solution of carbonate of soda; pectate of soda is thus formed by the action of the alkali upon the insoluble pectose contained in the vegetable tissue; and on mixing the solution with chloride of calcium a gelatinous pectate of lime is precipitated. This is to be well washed, and treated with dilute hydrochloric acid, which removes the lime, leaving the pectic acid as a transparent insoluble jelly.

If this jelly be long boiled with water it is gradually dissolved, and a deliquescent insoluble acid is the result (*parapectic acid*), which yields a precipitate with chloride of barium. Parapectic acid in its turn, when treated with alkalies, passes into another uncrystallizable acid, the *metapectic*, which has a strongly sour taste; it is no longer precipitable by chloride of barium, though it yields a precipitate with subacetate of lead.

According to Fremy, pectin is susceptible of a specific fermentation, produced by a peculiar substance which is present in the cellular tissue of the vegetable. This change is not attended by any disengagement of gas, but simply by the conversion of the soluble pectin into two gelatinous acids, which are insoluble in water: one of these acids he terms *pectosic acid.* It is almost insoluble in cold water, but becomes dissolved by boiling water, and the liquid gelatinizes on cooling. This acid appears to be the one formed in the first instance, but it gradually passes into a second, which is the pectic acid already described; the gelatinizing of many juices of fruits arises from the gradual conversion of the pectin which they contain into these gelatinous acids. The composition of these gelatinous bodies cannot be said to be established with certainty; since there is no means of determining whether or not they have been prepared in a pure condition, nor is it easy to procure them in a uniform state of desiccation. But whatever may be the true composition of these bodies, it is clear that pectose is readily susceptible of modification under the influence of acids, of alkalies, and of a peculiar ferment contained in the plant or fruit itself; and these modifications are probably connected with the assimilation or separation of the elements of water. None of these compounds exert any rotatory action upon polarized light, a character which indicates an important molecular distinction between them and the class of sugars. All these closely related bodies, it may be observed, contain oxygen in larger proportion than would be required to convert their hydrogen into water. When treated with nitric acid they furnish mucic and oxalic acids.

Fremy assigns to these different bodies the composition given in the following table, but the formulæ require confirmation:—

Pectose	Composition unknown.	Not gelatinous.
Pectin	$C_{64}H_{40}O_{56}$, 8 HO	Viscous.
Parapectin	$C_{64}H_{40}O_{56}$, 8 HO	Not gelatinous.
Metapectin	$C_{64}H_{40}O_{56}$, 8 HO	Not gelatinous.
Pectosic Acid . . .	2 HO, $C_{32}H_{20}O_{28}$, HO	Gelatinous.
Pectic Acid	2 HO, $C_{32}H_{20}O_{28}$	Gelatinous.
Parapectic Acid . .	2 HO, $C_{24}H_{15}O_{21}$	Not gelatinous.
Metapectic Acid . .	2 HO, $C_8H_5O_7$	Not gelatinous.

§ IV. CELLULOSE AND WOODY FIBRE.

(944) CELLULOSE ($C_{36}H_{30}O_{30}$).—If a thin slice of wood be examined under the microscope, it is immediately apparent that it

is not a homogeneous structure, but that it is composed of a cellular or fibrous substance, the texture of which assumes a different appearance, according as the slice has been cut across the grain of the wood, or parallel to it. This ligneous fibre, or true woody matter, consists, according to the researches of Payen, of two essentially distinct portions. One of these, which has received the name of *cellulose*, is the basement tissue, found in all vegetables; it is nearly pure in cotton, linen, elder pith, and in the pith of the *Aralia Papyrifera* (Hooker), from which *rice paper* is prepared; the other is a deposit of incrusting matter which lines the interior of these cellules in amorphous layers, varying in thickness according to the age or character of the ligneous substance.

Cellular tissue forms the groundwork of every plant, and when obtained in its pure state, its composition is the same, whatever may have been the nature of the plants which furnished it, though it may vary greatly in appearance and physical characters; thus it is loose and spongy in the succulent shoots of germinating seeds, and in the roots of plants, such as the turnip and potato; it is porous and elastic in the pith of the rush and the elder; it is flexible and tenacious in the fibres of hemp and flax; it is compact in the branches and wood of growing trees, and becomes very hard and dense in the shells of the filbert, the peach, the cocoa-nut, and the *Phytelephas*, or vegetable ivory. Vegetable cellular tissue, in its succulent form, is easily digestible, but where it has become compact and incrusted with true woody matter, as in the husks of the seed, and in the hard portions of the stems, and even when simply condensed into tenacious fibres, like those of hemp and flax, it is no longer digestible, or in a condition to serve as nutriment to the higher orders of animals.

It is scarcely possible to obtain cellulose in a state of purity from ligneous tissue by artificial means, since the incrusting woody matter, when once deposited within its meshes, is retained with great obstinacy; but it is presented in a pure condition in finely carded cotton, in linen, and in the finest kinds of filtering paper; to these sources the chemist usually has recourse when he desires to examine the properties of cellulose.

Pure cellulose is a white, tasteless substance, insoluble in water, alcohol, ether, or oils. It is heavier than water: its fibres are transparent, and exert a depolarizing influence upon a ray of polarized light. Cold concentrated sulphuric acid dissolves it, and produces a treacly liquid, converting it at first into dextrin, and subsequently into grape sugar. Weak acids exert but little effect upon cellulose, but the action of these and of all other solvents is materially greater upon the recently formed cellules than upon the old ones. Alkaline liquids when dilute do not act upon cellulose, but when concentrated they gradually destroy its texture. A solution of chlorine acts but very slowly upon cellulose.

Cellulose, in its natural state, is not coloured blue by iodine; but after it has been digested for a short time with sulphuric acid, it becomes of a fine blue when free iodine is added. This reaction is sometimes serviceable in the microscopic examination of vegetable tissues; cellulose being thus easily distinguished from tissues into the composition of which nitrogen enters. By the prolonged action of sulphuric acid, the property of being coloured blue by iodine disappears, the dextrin and sugar which are formed, not being susceptible of the blue coloration.

The reactions with nitric acid about to be described, show that the formula of this substance cannot be less than $C_{36}H_{30}O_{30}$.

(945) PYROXYLIN or *Gun Cotton* ($C_{36}H_{21}$, 9 NO_4, O_{30}, Hadow).—When cellulose in any form, such as cotton, tow, linen, sawdust, or paper, is dipped into a mixture of equal measures of oil of vitriol and of nitric acid of sp. gr. 1·520, no change of form ensues, but a remarkable chemical alteration takes place; a certain number of equivalents of hydrogen are abstracted, and an equal number of equivalents of peroxide of nitrogen (NO_4) supply their place. The fibre in undergoing this change becomes increased about 82 per cent. in weight (Hadow), and acquires completely new properties. In order to prepare this remarkable body, called *gun cotton* by its discoverer, Schönbein, 1 part of finely carded cotton is immersed in 15 parts of a mixture of equal measures of strong nitric acid (sp. gr. 1·5), and sulphuric acid (sp. gr. 1·845). The cotton must be completely immersed in the mixture, otherwise it becomes so hot as to undergo instant decomposition. After a few minutes' immersion it must be plunged into a large volume of cold water, and then washed, so long as the least trace of acid is perceived when the moist mass is placed upon litmus paper; it is then carefully dried at a temperature below 212°.

Pyroxylin, as thus prepared, scarcely differs from unchanged cotton in appearance; it is white and fibrous, rather harsh to the touch, and when examined by the microscope in a beam of polarized light, it is found to have lost the property of depolarization which ordinary cotton possesses. It is somewhat hygroscopic, but when dry it is an excellent insulator of electricity, and becomes highly electrical by the mere operation of pulling it out in the fingers. Pyroxylin is insoluble in water, alcohol, and dilute acids, but it is soluble in acetic ether and in acetate of methyl. Potash dissolves it freely, and the solution contains a quantity of sugar and a mixture of nitrate and nitrite, as well as of oxalate of potash. Ammonia, when mixed with ether, also dissolves it, and leaves it by spontaneous evaporation in a pulverulent form. The solution in potash contains a peculiar acid (resembling the saccharic), which yields an insoluble precipitate with acetate of lead. The alkaline solution of pyroxylin, when mixed with ammonia-nitrate of silver, and gently heated, reduces the silver in the form of a film upon the surface of the glass, producing a brilliant mirror-like surface; carbonic acid is disengaged with effervescence during the reaction upon the silver salt.

Strong sulphuric acid dissolves pyroxylin in the cold without the evolution of gas, and the liquid is not rendered turbid by dilution. If the pyroxylin be pure, the solution is colourless, but it is brown if any unaltered fibres of cotton remain in the mass. Nitric acid in the cold is without action upon it, but if the acid be heated, it gradually dissolves the pyroxylin, and on dilution deposits it again. By boiling it with the acid it is decomposed, red fumes escape, and dilution then causes no precipitate. Pyroxylin may be reconverted into ordinary cotton, according to the observation of Mr. Hadow, by digestion at ordinary temperatures in an alcoholic solution of hydrosulphide of potassium (KS, HS), and the change may be effected still more rapidly if heated with it. M. Béchamp found that a similar reduction takes place when the pyroxylin is acted upon by protochloride of iron.

The most remarkable property of pyroxylin is the facility with which it takes fire, and the rapid and complete manner of its combustion. In the open air it burns with a flash, but without either smoke or report; a temperature just below that of 400° is sufficient to inflame it, being nearly 200° less than that required to ignite gunpowder. In the open air, pyroxylin burns more rapidly than gunpowder, but if compressed so as to form a fusee, its rapidity of combustion may be reduced below that of powder, and the more it is compressed the slower is the combustion. If it be fired in a confined space it produces violent explosive effects from the suddenness of its combustion, and from the large quantity of gaseous matter which it furnishes. The extreme suddenness of its inflammation, and the short space of time during which its propulsive force is exerted, produce both greater strain upon the gun-barrel, and less effect upon the ball, in consequence of which it appears to be less eligible as a projectile agent than gunpowder. In certain cases, such as in mining operations in hard and brittle rocks, it may be beneficially employed, as it may be driven into borings above the head of the miner, and if mixed with nitre in quantity sufficient to convert the whole of the carbon into carbonic acid, it produces much less fume and noxious gases than gunpowder; in addition to which it has the great advantage of leaving no " train" by leakage from the vessels in which it is stored up. Exposure to damp and even prolonged immersion in water, produces no deterioration in the explosive quality of this compound when it is again dried.

During the combustion of pyroxylin a large volume of steam is generated, mixed with a variable proportion of carbonic acid, carbonic oxide, and nitrogen gases; traces of nitric acid and of cyanogen are also formed. Considerable difference prevails in the statements of different experimenters respecting its propulsive power as referred to that of gunpowder: all agree that weight for weight its explosive force is much greater, some say three times as great, others four times that of the best musket powder. According to the experiments of a Commission appointed by the French Government to examine the question, the explosive power appears in some measure to depend upon the degree of compression of the pyroxylin in the charge; as a mean result, the pyroxylin produced an effect equal to that of about three times its weight of gunpowder.

The results of Mr. Hadow's experiments, (*Q. J. Chem. Soc.*, vii., 208), serve to explain the conflicting statements relative to the properties and composition of this remarkable substance. It appears from this enquiry that the composition of gun cotton differs according to the degree of concentration of the acids employed in its formation, and that at least four different and definite compounds may be formed, having the following composition:—

$$A = C_{36} \left\{ \begin{matrix} H_{21} \\ 9\ NO_4 \end{matrix} \right\} O_{30}$$

$$B = C_{36} \left\{ \begin{matrix} H_{22} \\ 8\ NO_4 \end{matrix} \right\} O_{30}$$

$$C = C_{36} \left\{ \begin{matrix} H_{23} \\ 7\ NO_4 \end{matrix} \right\} O_{30}$$

$$D = C_{36} \left\{ \begin{matrix} H_{24} \\ 6\ NO_4 \end{matrix} \right\} O_{30}$$

When equal measures of the sulphuric and nitric acids [illegible] employed, each in the highest degree of concentration, the compound A is formed: it is highly explosive, soluble in acetic ether, and insoluble in any mixture of alcohol and ether. If the acids used be of a strength intermediate between $HO, NO_5 + 2\,(HO, SO_3) + 3$ aq, and $HO, NO_5 + 2\,(HO, SO_3) + 4$ aq, the compound B is produced: it is less explosive than A, is insoluble in acetic acid, but soluble in a mixture of seven parts of ether and one part of alcohol. Mixed acids of the strength $HO, NO_5 + 2\,(HO, SO_3) + 4$ aq, produce the compound C, which is largely soluble both in ether, and in glacial acetic acid: it is highly combustible, but scarcely explosive. The compound D is formed when acids containing five equivalents of water are used: it is soluble in ether and in glacial acetic acid: the ethereal solution on evaporation leaves an opaque white film; but the ethereal solutions of all the other varieties leave a transparent film when allowed to evaporate.

M. Béchamp (*Ann. de Chimie*, III., xlvi. 338), still adheres to the formula ($C_{24}H_{17}O_{17}, 5\,NO_5$) proposed by Pelouze, as representing gun cotton (the compound which contains the largest amount of NO_4); but his analytical results do not satisfactorily accord with the formulæ which he adopts, and cannot be reconciled with the occurrence of nitrite of potash in the solution which is formed when gun cotton is treated with a cold solution of the alkali.

Collodion.—The solution of pyroxylin in a mixture of ether and alcohol is known under the name of *collodion*. When this solution is exposed to the air for a few moments in the form of a thin layer, the solvent evaporates, leaving the pyroxylin as a transparent membranous pellicle. Collodion has been applied to excoriated surfaces, for the purpose of forming an artificial skin in order to protect them from the action of the air; but its most extensive application is in the preparation of a sensitive transparent surface for the reception of photographic images (884) by diffusion over plates of glass, after it has been duly impregnated with a soluble iodide. On immersing the film into a solution of nitrate of silver, the whole surface becomes impregnated with iodide of silver in the most favourable condition for the reception of photographic impressions. According to Mr. Hadow, the compound B is that which is best fitted for the preparation o photographic collodion. The temperature at which the compound is formed, has a very material influence upon the mechanical qualities of the collodion. If the temperature be not raised to 120 or upwards the solution is viscid and glairy, and does not diffuse itself readily over the glass. The successful preparation of a good photographic collodion requires attention to a number of minute precautions, many of which are detailed in the paper of Mr. Hadow already quoted.

(946) *Nitrous Derivatives from Sugar &c., allied to Pyroxylin.*—Other substances besides cellulose may be converted into bodies more or less analogous to pyroxylin, by the action of a mixture of nitric and sulphuric acids. Powdered cane sugar is converted by the same mixture of acids into a bitter yellowish mass of resinous appearance: it is very slightly soluble in water, and according to Sobrero contains $C_{12}H_9$, 2 NO_4, O_{11}. A somewhat similar compound may be formed from gum arabic, and also from milk sugar. If starch be treated with concentrated nitric acid it is rapidly dissolved, and if the viscid solution thus obtained be immediately diluted with water, a white tasteless insoluble precipitate is occasioned, termed *Xyloidin*, which appears to be a compound of starch and peroxide of nitrogen, $C_{12}H_8$, $2NO_4$, O_{10}, analogous to the foregoing. But the most remarkable body belonging to this class is one which is produced when mannite is acted upon by the mixture of nitric and sulphuric acids. It is insoluble in water, but is readily dissolved by boiling alcohol; the *nitromannite* (C_6H_4, 3 NO_4, O_6) crystallizes in fine needles as the solution cools. This compound explodes powerfully by a blow from a hammer. If gently heated it may be melted, but at a higher temperature than that required for its fusion, it explodes, and produces red vapours.

In all these cases it will be observed that the derivative nitrous compounds are produced by the substitution of a variable number of equivalents of hydrogen by an equal number of equivalents of peroxide of nitrogen; each equivalent of nitric acid, when acted upon by an equivalent of hydrogen derived from the organic body, yielding one equivalent of water and one of peroxide of nitrogen; $NO_5 + H = NO_4 + HO$. The water is absorbed by the sulphuric acid contained in the mixture; and the acid, after its action upon the organic compound, is found in all cases to have become diluted by the water thus removed from the body submitted to its influence. The addition of the sulphuric acid in these cases has two advantages, one being the removal of the water produced by the reaction; the other, the prevention of the solution of the new compound, and its further alteration by the nitric acid. A mixture of nitric and sulphuric acids is now frequently employed for the purpose of obtaining compounds in which NO_4 is substituted for hydrogen: nitroglycerin (C_6H_6, $2\,NO_4$, O_6; De Vrij) and various other compounds may be obtained in this manner with facility; the reaction however requires careful watching, as it is apt to become tumultuously violent, and sometimes, as in the case of nitroglycerin, the compounds which are formed are liable to explode during their preparation.

(947) Lignin.—The incrusting matter contained within the cellular tissue, which gives hardness to wood, is most abundant in the heart-wood of trees, and in the hard shells of many varieties of nuts. This substance appears to be a mixture of several proximate principles; it contains a larger proportion of hydrogen than cellulose, the proportion of oxygen being insufficient to convert the whole of the hydrogen into water. This incrusting matter does not appear to have a uniform composition in all woods. It is, however, always characterized by being soluble in alkaline liquids, though it is insoluble in water. Sulphuric acid chars it, and an aqueous solution of chlorine attacks and dissolves it. When submitted to distillation in close vessels, it evolves acetic acid; and it is found that the harder the wood, and the larger the proportion of this incrusting substance which it contains, the greater is the proportion of acetic acid which is furnished when equal weights of different woods are subjected to destructive distillation. When ligneous fibre is heated with hydrate of potash an oxalate and acetate of the base are formed.

The ligneous matter is generally deposited in a state of mixture with a variable quantity of resinous matters, which colour the wood and increase its inflammability. A certain proportion of saline matter is also contained in the deposited fibre, as well as small quantities of compounds containing nitrogen.

The applications of cellulose and of ligneous fibre in the arts are numerous and of great importance. Besides its every-day use in the form of wood, the fibre constitutes the basis of all linen, cotton, and hempen goods; and after these substances have ceased to be serviceable as textile fabrics, they are still, in the hands of the paper-maker, convertible into a material scarcely less valuable.

(948) *Paper-making.*—The rags which are employed in the manufacture of paper are sorted, according to the material of which they consist, into linen, cotton, hempen, and woollen, and are afterwards further separated into white, coloured, and black. The seams and knots are cut out, and the rags are then well

beaten to get rid of dust and dirt. Coloured rags can be employed in the preparation of writing-paper if they be first bleached by the action of chlorine, which is often applied to them in the gaseous form. For this purpose they are moistened, and placed on perforated shelves in wooden or stone chambers, into which the gas is transmitted. An excess of chlorine must be carefully avoided, as it is liable to enter into chemical combination with the fibre, and by displacing a portion of the hydrogen, to form a substitution compound, which, being destitute of tenacity, forms a brittle paper. Frequently, however, the rags, after having been reduced to the form of pulp, are bleached by means of chloride of lime. In all cases it is necessary to ensure the removal of the last traces of chlorine, which would not only cause the paper to become brittle, but when the paper is used for manuscript purposes, would gradually discharge the ink. The removal of the chlorine is effected by the addition of a small quantity of sulphite or of hyposulphite of soda; by which the chlorine is converted into chloride of sodium, and the sulphite into sulphate of soda, whilst sulphurous acid is set free:—

$$2\,(NaO,\,SO_2) + Cl = NaCl, + NaO,\,SO_3 + SO_2.$$

The rags having been partially cleansed, either in their bleached or unbleached condition, are reduced by mechanical means into a fibrous paste, or smooth uniform pulp, with water. This pulp is then extended over wire strainers in a layer of uniform thickness, which when drained forms a film of paper. If this be simply dried and pressed it forms *blotting*, or *filtering* paper, and is too porous to be used as writing-paper. In order to fit it for the ink, it is *sized*, or coated with a mixture of weak fine glue and alum, by which means it is rendered less permeable to water. Many manufacturers mix the size with the pulp before it is made into sheets, but in this case it is necessary to employ a size of a different description to that which is applied to the finished sheets. The size which is to be mixed with the pulp usually consists of a mixture of three parts of a resinous soap and two parts of starch, to which a small quantity of alum is added.

Of all the numerous materials which have been tried as the basis of paper, none has been found so well adapted for the purpose as linen rags. Straw has been used to some extent as a material for paper, and it was at one time thought, owing to the abundance and cheapness of this substance, that it might be made a valuable substitute for rags, the supply of which is becoming inadequate to meet the demand; but the loss of material, from its brittle nature, during the process of manufacture, and other unforeseen circumstances, more than counterbalanced the advantage gained from the abundance of the supply.

(949) *General Remarks on Starch and Woody Fibre.*—The facts already mentioned show the ready convertibility of the organised bodies, starch and lignin, into others which, though of organic origin, are yet devoid of structure, and therefore of a less complicated nature. In most cases great similarity exists in the ultimate constitution of these bodies, many having identically the same composition as those from which they are derived: others, if not identical, differ among each other only in the presence or absence of one equivalent or more of water. It is, therefore, not surprising that a gradual transition should occur from the elaborate arrangement of the dense and compact tissue of the wood into the comparatively loose texture and low organization of starch; the ligneous tissue undergoing modifications of density, which gradually diminish from the compact structure of the *lignum vitæ* to the spongy cells of the fungus, or lichen. The tissue of the Iceland moss, for example, presents a close analogy with starch; it is gradually disintegrated by boiling, it swells up to a gelatinous mass, and yields a magma colourable by iodine: thence we arrive at true starch, and gradually, as the organization of this body is broken up by the successive action of chemical agents, the addition of iodine produces a coloration less and less intense, until in the perfect formation of dextrin it disappears altogether; and at length in cane sugar, in place of the cellular structure, crystalline form becomes apparent.

(950) *On the Decay of Woody Fibre, and the means of preventing it.*—When wood in a moist state is exposed to the air, it gradually undergoes decomposition; a species of fermentation is occasioned by the nitrogenized constituents, in consequence of which oxygen is absorbed, carbonic acid and water are exhaled, and the wood crumbles down into a blackish brown, vegetable mould, called *humus, ulmin,* or *gein.* This decay occurs most rapidly in young spongy wood, as this contains a proportionately larger quantity of the albuminous substance than the harder and older portions.

These changes arise principally from the porous texture of the ligneous constituents, and the presence of a certain quantity of matter containing nitrogen, and closely resembling albumen.

Wood, especially when under the influence of atmospheric vicissitudes, is rendered liable to decay from the decomposition of its albuminous component; this circumstance favours the growth of lichens and fungi, and encourages the ravages of insects, to which the albuminous portions in particular afford the means of nutriment. It is obviously a matter of high importance to protect the wood, as far as possible, from these influences. A superficial coating of some substance, impervious to air and moisture, answers this object in great measure, so long as it is maintained entire. Such a coating is usually supplied by the application of layers of resinous or oily matter, which, if needful, may be thickened with metallic oxides; as in the ordinary processes of tarring and painting. But a more effectual method of preservation consists in steeping the wood, sail-cloth, cordage, or other similar materials, for a given time in certain saline solutions, among which one of corrosive sublimate is the most effectual. A solution of this salt, containing from $\frac{1}{80}$th to $\frac{1}{75}$th of its weight of the mercurial salt, is employed in Kyan's process for preserving wood from dry rot. The object is still more completely attained by the process of M. Boucheric. He cuts down the tree, and whilst the leaves in great measure remain attached to it, he at once immerses the lower extremity of the trunk in the saline liquid, which usually contains about 1 per cent. of raw acetate of iron, or of sulphate of copper. The sap continues to rise in the yet green wood, and carries with it the preservative agent into the minutest ramifications. It is not even necessary to cut the tree completely down; for it suffices nearly to sever the trunk close to the roots, and to make around the tree a sort of trough of clay, into which the solution is poured, and whence it is rapidly absorbed.

Products of the Decay of Woody Fibre.—When vegetable mould, or mouldered wood from the trunk of a decaying tree, is digested in a weak solution of potash or of soda, a brown liquid is obtained, from which, on the addition of an acid, a blackish brown precipitate is obtained. This precipitate is readily soluble in alkalies, and always retains a considerable proportion of nitrogen. It is regarded by Mulder as a mixture of three substances, none of which is crystallizable, but which he considers as compounds of water, or of water and ammonia, with three different acids, viz., 1. *Geic acid,* $C_{40}H_{12}O_{14}$; 2. *Humic acid,* $C_{40}H_{12}O_{12}$; and 3. *Ulmic acid,* $C_{40}H_{14}O_{12}$. These substances are obviously the product of vegetable matter in stages of decay more or less advanced. Mulder found the brown substances formed by the prolonged action of dilute acids at a boiling temperature upon sugar, to resemble the ulmic and humic acids from mould, both in composition and in properties. Besides these acids, Berzelius has pointed out the existence of two other allied bodies, which have received the names of crenic and apocrenic acids (from κρήνη, a spring); they have been found in many mineral waters, and accumulate in the ochry deposits that occur around the margin of ferruginous springs. *Crenic acid* (3 HO, $C_{24}H_{12}O_{16}$, Mulder) has also been found associated with ammonia in vegetable mould. It forms a yellow solution, which retains ammonia with obstinacy, and rapidly absorbs oxygen, becoming converted into *Apocrenic acid* (2 HO, $C_{48}H_{12}O_{24}$, Mulder); the latter acid forms a brown solution in water, and also retains ammonia strongly. Indeed, this property of retaining ammonia with obstinacy is a characteristic of those imperfectly defined acid products which are formed during the decay of ligneous matter, and it is connected in an important manner with the functions which they subserve in supplying nutriment to growing vegetables, towards the support of which they contribute largely.

By the decay of herbaceous and aquatic plants in marshy soils, a material somewhat similar to humus is formed, which accumulates in beds often of great depth and extent, constituting *peat bogs*. Dried peat is found upon analysis to yield a larger proportion of carbon than woody fibre; it likewise contains an excess of hydrogen over the oxygen.

The process of decay in ligneous tissue is liable to considerable variation, according as it is allowed to take place with free access of air, or is effected under water with but a scanty supply of oxygen from without. When the atmosphere has free access, Saussure found that the oxygen of the air is converted into an equal volume of carbonic acid, while at the same time a large quantity of water is evolved. According to Hermann, a small proportion of nitrogen is absorbed during the process, and ammonia is generated. The water produced is at the expense of the oxygen and hydrogen contained in the ligneous tissue, so that the mouldered product contains a larger proportion of carbon than the wood upon which the experiment was conducted.

If the moistened wood be excluded from air, a small quantity of carbonic acid is evolved during its decay, accompanied, as in the former case, with the separation of water; and under certain circumstances marsh gas (C_2H_4) is liberated in considerable abundance.

Coal and other Combustible Minerals.

(951) The foregoing facts connected with the gradual decay of woody fibre and vegetable tissue, have a special interest, not only in their bearing upon the value of vegetable matter as a manure, but also in reference to the origin of the enormous masses of fossil fuel which are stored up in the bowels of the earth, and which are the result of complicated chemical changes under variable circumstances of temperature, moisture, and pressure—acting either upon vegetables which grew upon the spot, as in peat bogs now in process of formation, or upon the debris of trees or plants drifted from a distance, and accumulated in particular localities, as is now occurring in the deltas of the Mississippi, and other large rivers.

These deposits of fossil combustible matter may be sub-divided into—1. Peat; 2. Fossil resins, or bitumen; 3. Lignites, or brown coal; 4. Bituminous, or caking coal; 5. Steam coal; and 6. Anthracite.

1. *Peat.*—The vegetable origin of this substance is at once evident on inspection. As a fuel it is far inferior to coal: when raised from the bed in which it is formed, it retains a large quantity of water, in consequence of which it is necessary to stack it in heaps, in which it is freely exposed to the air. Even after it has been thus left to dry for many months, it often retains a fourth of its weight of water, and yields a quantity of ash, ranging from 5 to 10 per cent. or upwards.

2. *Bitumen* and *Fossil Resins.*—These substances include *amber*, *retinasphalt*, *asphalt*, *retinite*, and many other allied bodies which are chiefly contained in the tertiary strata. In many instances they are the products of the action of an elevated temperature upon vegetable bodies; and when this is the case, they form irregular deposits which impregnate the strata around: under these circumstances, masses of igneous rock, such as basalt or trap, will be found in their immediate neighbourhood. In other cases the bitumens occur in regular beds, which appear to have been formed in a manner similar to the deposits of true coal. Many lignites likewise contain the bitumens and resins disseminated through them in small quantities. They are more or less soluble in alcohol, ether, and the essential oils. Although combustible they are not consumed as fuel. Asphalt is largely used in the preparation of an artificial paving material, and the finer kinds are employed in the formation of a species of black varnish or enamel for leather.

3. *Lignite, or Brown Coal.*—This species of coal generally retains its woody lamellar structure to a considerable extent, though in this respect there are great differences; as its name implies, it has a brown colour. When distilled in close vessels it yields a coke which does not cake together, and in which the original form of the fragments is preserved; the ash is less abundant than in peat. The true lignites occur in the tertiary strata.

4. *Bituminous or Caking Coal.*—This is the most highly prized variety of coal, and is the most abundant product of the British coal fields. It occurs above the old red and beneath the new red sandstone, in what geologists have termed from its presence, *the coal measures.* There are several varieties of bituminous coal: some, as those of the Scotch *parrot coal,* are of a brownish black colour, and a slaty structure; when heated in closed vessels they emit a large quantity of gaseous matter, and leave a coke which is but incompletely fused and coherent. The Lancashire *cannel coal* is another form, which is characterized by its conchoidal fracture, and the waxy lustre which it exhibits; it is of a dull brownish black colour, yields a good deal of gas, and leaves an imperfectly fused hard lustrous coke; these coals are highly prized as *gas coals.* *Newcastle coal* represents a third variety; it is of a full blue black colour, has a brilliant lustre, and a cubic fracture; it burns with a bright luminous flame, and is much valued as household fuel; it furnishes a coke which is much swollen, caked together, and possessed of a high lustre.*

5. *Steam Coal.*—This is a coal intermediate in quality between the bituminous coals and the anthracites; it burns freely and with flame, giving out a steady heat, but it does not yield sufficient volatile matter to be advantageously employed in the preparation

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* A remarkable bituminiferous deposit occurs amongst the coal measures in the neighbourhood of Bathgate near Edinburgh, which has been sold under the name of "Boghead Cannel Coal," and has been extensively employed to mix with inferior descriptions of coal which are employed in the manufacture of coal gas. It contains from 18 to 25 per cent. of an aluminous ash, which retains the form of the mineral when it is burned in the open fire; when distilled at a low temperature in closed vessels, the mineral gives off a very large proportion of liquid hydro-carbons mixed with a certain quantity of dense gaseous hydro-carbons. The mass left after distillation is remarkable for the small proportion of carbon (from 6 to 10 per cent.) which is left behind in the ash. A remarkable lawsuit arose upon the question whether or not this substance was to be regarded as a *coal.* The term coal, however, being one rather of popular than of scientific language, and not admitting of accurate definition, the opinions of the chemists, geologists, and histologists who were examined upon the question were divided, and the case was decided upon a collateral issue.

See account of [illegible] Albert Coal – [illegible] of coal gas. It is well fitted for use in the steam navy, since it does not crumble readily in the hold of a vessel during its rolling, and it emits but little smoke. It furnishes a coke which scarcely cakes together, and which possesses but little coherence or lustre. Much of the Welsh coal is of this description.

6. *Anthracite.*—The *stone coal*, or *culm*, as this variety is sometimes called, is found in the lowest portion of the carboniferous strata. It contains but a very small portion of volatile matter, burns almost without flame with a steady red glow. When heated, it splinters into small fragments, a circumstance which often occasions considerable inconvenience in its application as a fuel. The most compact forms burn indeed with great difficulty. This coal is black; it has a high lustre, and often exhibits an iridescent play of colours; its fracture is lamellated parallel to the bed from which it was taken, but the cross fracture is oblique or conchoidal. The coke obtained from it differs little in appearance from the original coal either in bulk or in weight. Anthracite is extremely abundant over vast tracts of North America, but much of it is so compact that it is scarcely applicable as a fuel. A large quantity of excellent anthracite is obtained from the South Wales coal field.

The subjoined tables will give an idea of the composition of wood, and will illustrate the progress of its decay. They also furnish a synoptic view of the composition of some of the principal varieties of coal, in the order of their occurrence in successive geological stages. The proportion of oxygen, it will be seen, diminishes rapidly, and that of the hydrogen more slowly, as the coal passes from lignite towards anthracite, in which form it consists of nearly pure carbon.

The amount of ash in coal is very variable. In the finest species of coals the fixed ash appears to be disseminated pretty evenly through the mass, but in the coarser varieties, thin seams of iron pyrites, and at other times, as in the Newport coal, crystallized laminæ composed of the mixed carbonates of lime, magnesia, and protoxide of iron are found. It is obvious that where these seams occur, their components must have been carried into the mass by infiltration. The ash of pure coal furnishes but minute quantities of the salts of the alkalies; it usually contains but little lime or magnesia, the bulk of it consisting of silicate of alumina, with variable amounts of oxide of iron. Vaux also found traces of copper and lead in most of the coals which he analysed.

Composition of Wood and Coal.

Variety. .	Oak,	Oak,	Humus, from		Peat.		Asphalt.	Lignite.		
Locality, &c.	Wood.	Decayed.	Decayed Oak.		Dartmoor.	Vulcaire.	Mexico.	Bovey.	Dax.	Boghead.
Authority .	W.A.M.	Liebig.	Meyer.	Will.	Vaux.	Regnault.	Regnault.	Vaux.	Regnault.	W.A.M.
Specif. gr. .	0·81				0·849		1·063	1·129	1·272	1·196
Coke . .	21·3				29·30		9·0	30·8	49·1	30·23
Carbon . .	50·10	53·47	54·0	56·0	54·02	56·25	78·10	66·31	69·52	63·10
Hydrogen .	6·07	5·16	5·1	4·9	5·21	5·63	9·30	5·62	5·59	8·91
Nitrogen .					2·30			0·56		
Oxygen .	43·68	41·37	40·9	39·1	28·17	32·54	9·80	22·86	19·90	7·25
Sulphur .					0·56			2·36		0·96
Ash . . .	0·15				9·73	5·58	2·80	2·27	4·99	19·78
The same ash free										
Carbon . .	50·18				59·73	59·57	80·34	67·85	73·18	78·67
Hydrogen .	6·08				5·91	5·96	9·57	5·76	5·88	11·11
Nitrogen .					2·54	2·09		0·58		
Oxygen .	43·74				31·82	32·38	10·09	23·39	21·14	10·22

Composition of different varieties of Coal.

Variety	Parrot.	Cannel.	Caking.	Dry.	Do.	Steam.	Anthracite.	
Locality	Lesmahagow.	Wigan.	Newcastle.	Wolverhampton.	St. Helen's.	Newport.	S. Wales.	Pennsylvania.
Authority	W.A.M.	Vaux.	Richardson	Vaux.	Vaux.	W.A.M.	Vaux.	Regnault.
Specific gravity . .	1·251	1·276	1·280	1·278	1·279	1.309	1·392	1·462
Coke	43·3	60·36		57·21	65·5	75·1	92·1	89·5
Carbon	73·44	80·07	86·75	78·57	75·80	81·47	90·39	89·21
Hydrogen	7·62	5·53	5·24	5·29	5·22	4·97	3·28	2·43
Nitrogen	11·761	2·12	6·61	1·84	1·92	1·63	0·83	3·69
Oxygen		8·08		12·88	10·99	5·32	2·98	
Sulphur	1·145	1·50		0·39	0·90	1·10	0·91	
Ash	6·034	2·70	1·40	1·03	5·17	5·51	1·61	4·67
Carbon	78·16	82·29	87·97	79·38	79·93	86·27	91·87	93·59
Hydrogen	8·11	5·68	5·31	5·34	5·50	5·26	3·33	2·55
Nitrogen	13·73	2·18	6·72	1·86	2·03	1·73	0·84	3·86
Oxygen		8·31		13·02	11·58	5·54	3·01	

§ V. On Fermentation.

(952) Under the term fermentation, frequent mention has been made of a particular change which saccharine bodies undergo, in consequence of which they become converted into carbonic acid and alcohol. Many other substances, however, besides sugar, are susceptible of an analogous change, and the term *fermentation* is now applied to various transformations which organic compounds experience under the influence of a small quantity of organized matter, which is itself in a state of active alteration. This active substance, which is termed a *ferment*, neither imparts anything to, nor receives anything from, the substance which is undergoing fermentation. During this change, the body which is experiencing fermentation is gradually broken up into two or more substances of simpler composition; in certain cases the elements of water are assimilated, in others they are separated, whilst in a third class of decompositions water is neither separated nor assimilated.

For example, when fruit sugar is placed in contact with ordinary yeast, the sugar is simply converted into carbonic acid and alcohol, the yeast acting as the ferment:—

$$\overbrace{C_{12}H_{12}O_{12}}^{\text{Fruit Sugar.}} \text{ gives } \overbrace{4\ CO_2}^{\text{Carb. Acid.}} + \overbrace{2\ (C_4H_6O_2)}^{\text{Alcohol.}}.$$

No assimilation or separation of water occurs in this case. But when grape sugar, $C_{12}H_{14}O_{14}$, is subjected to fermentation, carbonic acid and alcohol are formed as before, and two equivalents of water are eliminated:—

$$C_{12}H_{14}O_{14} = 4\ CO_2 + 2\ (C_4H_6O_2) + 2\ HO.$$

Again, when cane sugar is submitted to fermentation, it assimilates one equivalent of water, first becoming changed into fruit sugar, and this substance is afterwards broken up into carbonic acid and alcohol as before;

$$C_{12}H_{11}O_{11} + HO = C_{12}H_{12}O_{12}, \text{ and } C_{12}H_{12}O_{12} = 4\ CO_2 + 2\ (C_4H_6O_2).$$

The different varieties of fermentation receive their distinctive name from the principal products which they furnish: for example, when spirit of wine is formed from sugar, the change is called the *alcoholic* or *vinous* fermentation; when lactic acid is converted into butyric acid, the process is termed the *butyric* fermentation, &c.

In all cases of fermentation the following conditions are essential:—1, the presence of water; 2, a temperature ranging from 50° to 90°; 3, a peculiar ferment (the nature of which varies in the different cases); 4, the body which is to undergo fermentation. It may be remarked, that in most instances the compounds susceptible of fermentation are crystallizable products. It is especially to be observed, although the ferment does not contribute any of its components to the results of fermentation, yet that it is itself destroyed during the operation; the products of its decomposition being generally discernible mixed with the results of the fermentation. This fact has an important bearing upon the theory of the process, but its significance will be best understood by tracing the operation through its different stages in the formation of alcohol.

(*a*) *Alcoholic Fermentation.*

(953) When the juices of plants or of fruits containing sugar, such for instance as *must* (the juice of the grape), are kept at a temperature of about 70° for some hours, a change begins to show itself. The liquid becomes turbid, and small bubbles rise to the surface; or in popular language, it begins to *work* or to ferment. This change is due in the first instance to the alterations produced in the albuminous and azotised matters, which all such juices contain, under the combined influence of atmospheric oxygen, warmth, and moisture. This azotised matter is decomposed, and an intestine change commences, which after it has once begun, continues in vessels from which the further access of air is prevented. As the fermentation proceeds a continual disengagement of heat is maintained, whilst a constant extrication of gas continues; this gas, if collected, is found to consist entirely of carbonic acid. After a time the escape of gas diminishes, and at length ceases; if the liquid be now examined, the sweet taste of the sugar will have disappeared, and the solution will have acquired a flavour more or less spirituous. If this liquid be distilled, the first portions that come over will be found to contain an inflammable product lighter than water, which is easily recognised as dilute spirit of wine or alcohol.

(954) *Properties of Yeast.*—Upon examining the liquid which remains after fermentation is complete, it is found to contain a multitude of small oval organized bodies which do not exceed $\frac{1}{2500}$th of an inch in diameter, and which when viewed under the microscope, are seen to consist of nucleated cells presenting the appearance shown in fig. 332, page 106. These cells form the essential constituent of *yeast*, which is obtained in great abundance during the fermentation of wort in the manufacture of beer.

Yeast is the substance which possesses, in the highest degree, the power of producing the alcoholic fermentation. Its efficacy in this respect is easily proved by the following experiment:—Dissolve 4 parts of pure cane sugar in 20 parts of water, and add 1 part of fresh yeast; then expose the mixture to a temperature of about 80° F. In less than an hour fermentation will commence, and carbonic acid will be evolved in abundance.

Yeast, when in its active condition, always exhibits a slightly acid reaction; if thoroughly washed, the globules are much less active, but they again acquire activity by exposure for a few hours to the air, during which time the acidity is again developed. The addition of a minute quantity of some of the vegetable acids, such as the acetic or the tartaric acid, to washed yeast, immediately restores its activity, but if a larger quantity of the acid be employed the process of fermentation is arrested. The strong mineral acids, particularly the sulphuric acid, when present even in very small quantity, also immediately put a stop to the alcoholic fermentation. It is also completely checked by the addition of a small quantity of free alkali. Many other circumstances likewise put an immediate stop to the process of fermentation. For example:—A solution which contains more than one fourth of its weight of sugar, cannot be made to ferment; the presence of 20 per cent. of alcohol or upwards, also puts an end to the process: the addition of a strong solution of common salt, or the presence of many metallic salts in the liquid, such for instance as nitrate of silver, corrosive sublimate, and sulphate or acetate of copper, check it immediately. The occurrence of fermentation is also prevented by the presence of small quantities either of oxide of mercury, of strychnia, or of quinia, as well as by solutions containing traces of sulphurous acid or of the sulphites. Small quantities of kreasote, of oil of turpentine, and of many other essential oils, have a similar effect.

On the other hand, according to Quevenne, neither solution of arsenious acid, of acetate of lead, nor of tartar emetic exert any retarding effect upon the progress of fermentation. If yeast be boiled for a few minutes, it is deprived of its power of exciting fermentation. Yeast may be dried at a low temperature or by pressure, and preserved in this condition without losing its activity.

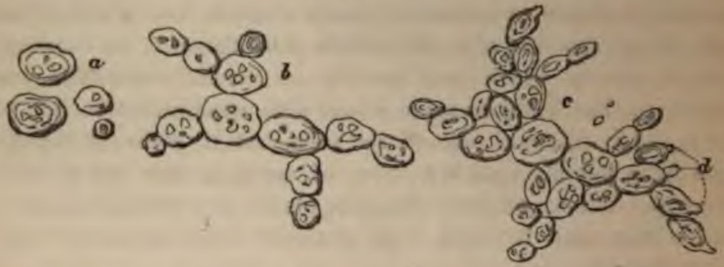
The part which the globules of yeast perform in exciting fermentation is extremely obscure. It is, however, certain, that the sugar ferments only in those points which are in actual contact with the globules. This fact is shown by the following instructive experiment of Mitscherlich:—Over one extremity of a wide tube open at both ends a piece of filtering paper is tied, and this covered extremity is plunged into a weak solution of pure cane sugar; the liquid quickly penetrates the paper and rises in the tube, which may be supported so as not to touch the bottom of the jar of syrup; if a small quantity of yeast be now introduced into the tube, and the whole be set aside in a warm place, fermentation will be found to commence in a few hours; but it will be confined to the portion of liquid within the tube, *i. e.*, to those portions of syrup which are actually in contact with the yeast globules. The bibulous paper allows free communication between the liquid within and without the tube, but it prevents the globules from passing into the mass of syrup in the outer vessel. These globules appear to be fungi or plants, of a very low degree of organization, and as such, their particles are continually undergoing change.

Varieties of Yeast.—According to the observations of Mitscherlich, who has carefully watched the development of the yeast plant under the microscope, there are two modifications of yeast: viz., *oberhefe* (surface yeast), and *unterhefe* (sediment yeast); these two varieties are propagated in different ways, and each produces specific results upon the fermenting liquid.

The *unterhefe* is the ferment of the Bavarian beer, which is allowed to ferment very slowly and at a low temperature; the formation of acid bodies, such as the lactic and acetic acids, is thus avoided, and the beer is more highly esteemed from their absence. The *unterhefe* consists of isolated globules of very varying dimensions. It appears to be propagated by spores thrown out from the larger cells, and not by buds and offshoots as is the case with the surface yeast; the temperature must not be allowed to rise beyond 45° nor to fall below 32° F.

Surface yeast is developed at a temperature varying from about 70° to 80°, and is the more active of the two forms in producing the alcoholic fermentation. The development of the yeast globules may readily be watched under the microscope by placing a drop of some saccharine infusion, such as wort, between two plates of glass, with a minute quantity of yeast. The granules will at first exhibit the appearance shown at *a*, fig. 332, where they can be seen to possess an outer cell wall, within which is a quantity of granular matter. In the course of a few hours some of these cells throw out buds such as are shown at *d*. The rapidity with which this development takes place, when it has once commenced, is often very great; *b* indicates a group of these bodies, probably all developed from the large central cell; *c d* shows the same group three hours later: within nine hours after it was first observed an oval patch of cellules had been formed, containing between seventy and eighty separate cells, in which the original cell was distinctly visible in the centre, and around it were grouped the new cells, decreasing in size towards the circumference; each of these cells contained the granular matter above spoken of, and fresh buds continued to form upon the exterior margin of the outer cells. The yeast cells frequently assume a more elongated form, flattened at the sides, but they continue to be developed in the same manner; both varieties may often be seen side by side under the microscope at the same time. The walls of these cells consist of a thin membrane which has the same composition as cellulose (Mulder); and within this membrane is an azotised gelatinous mass which here and there exhibits a kind of granular nucleus. This granular matter is soluble in acetic acid, and may thus without difficulty be separated from the cell membrane in which it is contained; it may then be precipitated for examination, by neutralizing the solution with carbonate of ammonia. The contents of the granules may also be extracted by means of a weak solution of potash, and can be precipitated by neutralizing it with acetic acid. When thus obtained, the precipitate has the properties and composition of protein.

FIG. 332.



Everything that destroys the vitality of these organized bodies destroys their power of exciting fermentation: for this reason too high a temperature stops the operation, and a depression of temperature also temporarily arrests it, though it is stated that even after exposure to a cold of 10° F. the fermentation is renewed when the temperature is allowed to rise.

The multiplication of the globules of yeast does not take place in solutions of pure sugar: on the contrary, during the process of fermentation, the granules undergo a gradual disintegration. For the decomposition of 100 parts of sugar, between two and three parts of yeast, calculating it in its dry state, are required. If the proportion of sugar to the yeast exceed this, the excess of sugar remains unaltered in the liquid; and if the cells be examined after fermentation has ceased, many of them will be seen to be ruptured and destroyed; and a certain quantity of lactate and acetate of ammonia, and other ammoniacal salts will be found in the solution.

Mitscherlich gives the following as the composition of ordinary washed yeast; first, when in a condition to excite fermentation, and secondly, in the partially exhausted state, after fermentation had ceased; in both cases the ashes have been deducted:—

	Entire cells.	Spent yeast.
Carbon	47·0	47·6
Hydrogen	6·6	7·2
Nitrogen	10·0	5·0
Sulphur	0·6	
Oxygen	35·8	

In this experiment the nitrogen in the spent portion was reduced to one-half of its former amount. This spent yeast, however, still contained an excess of active granules; but if entirely exhausted, it would furnish scarcely any nitrogen on analysis.

The inorganic matter contained in yeast amounts to a considerable quantity, not less than about 7·5 per cent. of the dried yeast. It consists entirely of phosphates of potash, soda, lime, and magnesia (Mitscherlich).

But although the yeast globules do not multiply in a solution containing pure sugar, they become rapidly developed in all saccharine vegetable infusions during fermentation, and multiply at the expense of the azotised matters which these liquids always contain, and which form an essential part of the nutriment of the yeast plant. Owing to this cause the quantity of yeast is increased to six or eight times its original amount during the fermentation of beer.

The following analyses by Messrs. Graham, Hofmann, and Redwood (*Q. J. Chem. Soc.*, v. 237), show that during fermentation the azotised matters in the liquid are reduced in quantity, whilst the yeast plants are becoming developed:—Pale malt wort, of sp. gr. 1088, which contained about 21 per cent. of solid matter before fermentation, yielded 0·217 per cent. of nitrogen, which would correspond to 3·43 per cent. of albumen: after full fermentation and removal of the yeast, the nitrogen amounted only to 0·134 per cent.;

this was no doubt partly in the form of ammoniacal salts, but if all were calculated as albumen, it would amount only to 2·11 of that substance.

The composition of the contents of the granules of yeast has already been stated to bear a close relation to that of albumen. This circumstance may afford some clue to the remarkable fact that yeast is never furnished except by the decomposition of albuminous matters. Various bodies which contain nitrogen furnish it when they have once begun to decay. Thus white of egg, muscular tissue, and cheese, during decomposition in the presence of saccharine solutions produce these globules, and true fermentation begins.

(955) *Progress of Fermentation.*—Much interesting information relative to the changes which solutions of sugar of various kinds undergo during fermentation may be obtained by examining them at intervals by means of a beam of polarized light. If a solution of starch sugar be mixed with yeast, the right-handed rotation which such sugar possesses in its natural state slowly diminishes, in a degree proportioned to the quantity of sugar which has undergone fermentation (Mitscherlich). But if a solution of fruit sugar or of *inverted* cane sugar (929), be watched in like manner from time to time, the phenomena are more complicated; the left-handed rotation undergoes no decrease until about three-fifths of the sugar has been decomposed, after which the rotatory power rapidly diminishes as the fermentation proceeds, but there is *no inversion* of the rotation. Dubrunfaut, who made these observations, remarks that this uncrystallizable sugar must consist of a mixture of at least two, and possibly of more modifications of sugar; one of which is neutral and is that which is first fermented, the other is possessed of left-handed rotation, and does not undergo fermentation until the neutral sugar has all been decomposed.—(*Ann. de Chimie,* III., xxi. 172.)

It has been already mentioned that when cane sugar is subjected to the vinous fermentation, it undergoes a preliminary change in consequence of the necessity of assimilating an additional equivalent of water. Owing to this circumstance, a much larger quantity of yeast is required in order to produce the fermentation of sucrose or cane sugar than is needed either by fructose or by glucose. It has been observed by Dubrunfaut, that if a solution of cane sugar which has been mixed with yeast be examined by polarized light before fermentation commences, the rotatory power upon polarized light will be inverted, and it will be found to have become left-handed, showing that the cane sugar has assumed the additional equivalent of water which it needed, and has thereby become converted into uncrystallizable fruit sugar. The same change is also strikingly shown by the increase in density which a solution of cane sugar undergoes previous to entering into fermentation. This circumstance was pointed out by Messrs. Graham, Hofmann, and Redwood, in their researches upon the decrease in density which saccharine solutions undergo during fermentation. (See their "Report upon Original Gravities," *Quart. Journ. Chem. Soc.*, v. 232.)

It was ascertained by these chemists that when quantities of cane sugar, starch sugar, caramel, and dextrin, which contained equal quantities of carbon, were dissolved in water and diluted till the solutions were equal in *weight*, the density of these solutions varied greatly, as will be evident on inspecting the following table: from which it appears on comparing together quantities of the different solutions, equal weights of which contain equal quantities of carbon, that starch sugar furnishes the densest solution; next to this comes malt wort, which owes its sweetness to starch sugar; then comes cane sugar; whilst dextrin gives a solution of smaller specific gravity; and caramel a solution the least dense of any of the substances compared together:—

Parts of Cane Sugar in 100 of solution.	Starch Sugar.	Pale Malt Wort.	Cane Sugar.	Dextrin.	Caramel.
25	1010·4	1010·0	1010·1	1009·7	1008·7
50	1020·8	1020·3	1020·2	1019·3	1017·3
75	1031·3	1030·6	1030·2	1028·8	1026·2
100	1042·4	1041·2	1040·6	1038·3	1034·9
125	1053·5	1052·1	1051·0	1047·9	1043·8
150	1064·9	1063·0	1061·8	1057·3	1052·8
175	1076·0	1074·2	1072·9	1066·9	1062·3
200	1087·8	1085·5	1083·8	1077·6	1071·8
225	1099·4	1097·2	1095·2	1086·3	1081·3
250	1111·4	1109·0	1106·7	1095·8	1091·0

Suppose for instance that 175 grains of cane sugar were dissolved in water, and the solution diluted till it weighed 1000 grains; it would have a sp. gr. of 1072·9. This solution if converted into starch sugar would become increased in specific gravity: so that a solution of starch sugar which contained in 1000 grains of the liquid a quantity of this sugar which would be furnished by the amount of cane sugar contained in the first solution, would have, as is represented in the second column, a specific gravity of 1076.

In a direct experiment, made for the purpose of observing this effect, it was found that a solution of cane sugar, to which a sufficient quantity of yeast had been added to effect its fermentation, and which at first had a sp. gr. of 1055, became in the course of an hour of a sp. gr. of 1058, though no fermentation had set in. In another experiment, a solution of sp. gr. 1055, containing $\frac{1}{300}$th of its weight of yeast, became increased in four days to a sp. gr. of 1057·9, although no appearance of fermentation, or of other change, was manifest.

When sugar is fermented, it is assumed in theory to be wholly converted into carbonic acid and alcohol; but in practice this is never the case. It was found by the chemists just quoted, in three careful experiments on the fermentation of cane sugar, in which one and a half, three, and six measures of yeast were respectively added to 100 measures of the syrup, that 4·4, 3·7, and 3·72 per cent. of the sugar were converted into a brown soluble substance resembling caramel, and at the same time a little free lactic acid was formed.

(*b*) *Fermentation of Bread.*

(956) *Composition of Bread Stuffs.*—The fermentation which takes place during the manufacture of bread was formerly supposed to be of a different nature to that which occurs during the preparation of alcohol, and it was therefore described under a distinct name, as the *panary* fermentation. It is, however, merely a modification of the alcoholic fermentation, which is produced by the action of the yeast upon the saccharine matter, which is either naturally present in the flour, or is developed by the action of the ferment on the starch. The chemical process of baking, however, cannot be rightly understood without a knowledge of the ordinary composition of the principal varieties of flour employed in the preparation of bread.

When corn is ground in a mill, the grain is reduced to powder, which may be separated by sifting into two principal portions—*flour* and *bran*. The bran is composed of the brownish coloured outer covering of the grain, which is tougher and harder than the internal portions, and consequently is not reduced by grinding to so fine a state of division: the flour is produced by the pulverization of the inner portion of the grain.

The most important constituents of the varieties of corn used as food are—1. starch; 2. gluten, a peculiar substance allied to albumen, which confers the tenacity and toughness upon dough; 3. a small proportion of sugar,* or of dextrin; 4. a little oily matter; 5. a small quantity of saline matter; and 6. a skeleton of ligneous tissue, which is the only portion of the seed not susceptible of digestion in the stomach. The proportions in which these ingredients are present in some of the principal varieties of grain used as food may be seen in the subjoined table. They vary, however, considerably in the same grain when grown in different climates. The proportion of gluten contained in wheat grown in the southern parts of Europe, and in the north of Africa, is considerably higher than in the best English-grown wheat; and the hard thin-skinned wheats furnish a larger proportion of gluten than the softer varieties of the grain.

	Whole wheat meal.			Maize.	Decorticated Rice.	Rye.	Peas.
	Polish.	Hardy White.	Algerian.				
Authority . .	Péligot.			Boussingault.			
Water . . .	15·2	13·6	13·6	17·1	7·3	14·7	8·6
Starch . . .	61·3	60·8	59·8	59·0	83·0	65·1	56·9
Dextrin and Sugar . .	6·3	10·5	6·4	1·5			
Azotised matter soluble	1·6	2·0	1·6	12·8	7·5	12·5	25·0
Azotised matter insol.	12·7	10·5	14·4				
Oily matter .	1·5	1·1	1·1	7·0	0·7	2·0	2·2
Fibre . . .		1·5	1·4	1·5	1·0	3·3	4·4
Salts . . .	1·4		1·7	1·1	0·5	2 4	3·1
	100·0	100·0	100·0	100·0	100·0	100.0	100 2

	Bran of soft French Wheat.	Barley. Fresenius.	Hopetown Oats. Norton.
Water	13·9	13·90	12·80
Starch	51·0	48·06	56·89
Dextrin and		3·87	1·83
Sugar		3·75	3·93
Gluten or its equivalent	14·9	13·18	16·29
Oily matter	3·6	0·34	4·74
Fibre	9·7	13·34	1·03
Salts	5·7	3·56	2·49
	98·8	100·00	100·00

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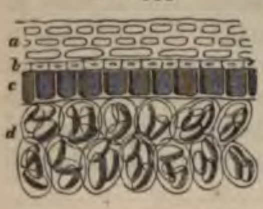
* M. Péligot considers that he has proved that sugar does not exist ready formed in the grain, or in the freshly ground flour. He was unable to distinguish its presence when the aqueous solution of the flour was examined by optical means, and he did not find that lime was dissolved more freely by this solution than by pure water. If sugar were present, the lime should have been dissolved in proportion to the quantity of sugar in the liquid.

The principal portion of the woody fibre is accumulated in the bran; but this substance likewise contains a large proportion of nutritive matter, for both gluten and oily matter are deposited in its cells more abundantly than in any other part of the grain; as may be seen by the result of its analysis, given above. Fig. 333 shows a section of part of a grain of rye, highly magnified, *a* indicating the cells forming the outer coat of the seed; *b*, a single row of cells forming the inner seed coat; *c*, a layer of cells containing gluten, (these three together form the bran;) *d*, the white inner part of the seed filled with starch granules, lodged in the meshes of the cellular tissue.

Fig. 333.



(957) Gluten.—This characteristic ingredient in the cereal seeds may be obtained in a separate form by mechanical means. The flour is made into a paste or dough, with water, and placed in a bag of fine linen, in which it is kneaded in a gentle stream of water so long as the washings have a milky appearance; the starch is by this means removed in suspension in the water, and the sugar and the dextrin are dissolved. A grey, sticky, tenacious, tasteless substance, resembling bird-lime in appearance, is left upon the cloth, consisting mainly of gluten, mixed with small quantities of bran and starch, and traces of oily matter. When dry it forms a hard, brownish, horny-looking mass. The gluten obtained from wheat and from rye possesses a peculiar tenacity, which is not observed, to anything like the same extent, in that obtained from the other cereals, and it is this tenacity of the gluten which especially fits the flour of wheat and rye for conversion into bread. Gluten is soluble in cold acetic acid, and in weak solutions of potash or of soda. It may be precipitated unchanged from either of these solvents by neutralizing them exactly with an acid. The dilute mineral acids combine with gluten and form a compound which is insoluble in excess of the acid. Gluten in its moist state rapidly putrefies, ammonia is formed, whilst hydrogen and carbonic acid are evolved, and the mass acquires the smell of decaying cheese. Gluten, however, cannot be regarded as a single definite body; it consists of at least two distinct substances, one of which is soluble in hot alcohol, whilst the other remains undissolved when treated with this menstruum. This insoluble portion is regarded by Liebig and by Dumas as vegetable fibrin. As the alcoholic solution cools, it deposits flocculi, which have the compo-

sition and properties of casein. A third substance still remains in the alcoholic liquid, and gives to this solution a syrupy or gelatinous consistence. On the addition of water, a white substance resembling albumen is precipitated; Dumas and Cahours have termed it *glutin:* on treating it with ether a small quantity of fat is extracted, and it is left in a state of purity: it may be dissolved by strong hydrochloric acid, and communicates to it a violet tint. It is, therefore, obvious that raw gluten contains several azotised principles, which differ considerably in chemical properties, though, as will be seen by the subjoined table, they are closely allied in ultimate composition:—

	Dumas and Cahours.			Bence Jones.
	Gluten Fibrin.	Gluten Casein.	Glutin.	Crude Gluten.
Carbon	53·23	53·46	53·27	55·22
Hydrogen	7·01	7·13	7·17	7·42
Nitrogen	16·41	16·04	15·94	15·98
Oxygen and Sulphur	23·35	23·37	23·62	21·38
	100·00	100·00	100·00	100·00

(958) *Preparation of Bread.*—In the preparation of bread, the flour is usually mixed with about half its weight of water, but the proportion varies with the quality of the flour. It is then thoroughly kneaded into a stiff paste, or dough, with the addition of a small quantity of yeast and a little salt, and put aside, at a temperature of about 70°, for some hours. The mass swells up, or, as the baker terms it, the *sponge* rises; that is to say, the sugar in the dough is decomposed by the yeast; carbonic acid is set free at all points of the mass, and, being imprisoned by the tenacious nature of the dough, the gas causes it to swell and become porous. At this stage it is cut into pieces of suitable size, and is put into an oven heated to a point between 450° and 550° F.; the heat causes the imprisoned air to expand still more, and gives the lightness of texture which characterizes good bread. On the application of heat to the dough, part of the water is expelled, 117 parts of dough yielding 100 of bread; the granules of starch become converted into the pasty, or gelatinous condition; the temperature of the crumb never exceeds 212° F., but the external surface of the loaf gradually becomes dry and hard, and losing a portion of its chemically combined water, is partially converted into a substance

allied to caramel (926), thus forming the *crust*. The bread is in this manner permanently fixed in the shape which it has acquired. During this baking, the alcohol formed by decomposition of the sugar, which corresponds in quantity to that of the carbonic acid, is expelled: some years ago a baking company was formed, in whose operations the collection of this spirit formed an important object. This end was attained by performing the baking in closed ovens, furnished with a still head for collecting and condensing the vapours. The project was, however, soon abandoned, and failed as a commercial speculation, owing in great measure to the dry unpalatable nature of the bread produced.

The French frequently employ *leaven* as a ferment instead of yeast. Leaven is dough kept from a previous batch for twenty-four hours in a warm place, till it has begun to undergo fermentation spontaneously. The decomposition which has commenced in the leaven spreads through the fresh mixture into which it is kneaded. In England a species of unfermented bread has lately been manufactured to some extent; in this case also the sponginess is given to the dough by means of carbonic acid, which is set free by the action of hydrochloric acid on carbonate of soda; common salt, a necessary ingredient in bread, being formed during the reaction, and a species of bread is obtained, which, as might be expected, is sweeter than ordinary bread, but not so light. According to Dr. Pereira, a good bread of this description may be obtained by mixing the materials in the following proportions:—

Wheat flour	7 lb.
Carbonate of soda . . .	350 to 500 grains.
Water	2¾ pints.
Hydrochloric acid . . .	420 to 560 grains.

The soda and flour are first intimately mingled, and then made into dough with the mixture of acid and water. If the soda be not equally and thoroughly distributed, it is detected after the baking, by the formation of a yellow spot around any portions of it that have escaped neutralization. Sponginess and lightness of texture are sometimes given to pastry by the employment of sesquicarbonate of ammonia, which is mixed with the dough instead of yeast: on the application of heat, the salt is expelled in the gaseous state, and by its expansion mechanically produces the desired effect.

In the latter case it is not improbable that the alkaline nature of the salt has an important influence upon the quality of the paste. Liebig (*Annalen*, xci. 246) has observed that in certain cases the employment of lime water in the manufacture of bread may be resorted to with great advantage. In order to understand the effect thus produced, it must be remembered that the peculiar toughness and elastic quality possessed by the dough furnished from the flour of certain of the cerealia, is dependent upon the gluten which they contain. It has been observed, that when gluten is kept in a moist state it undergoes a change in properties, in consequence of which it slowly loses its soft, elastic, and insoluble condition. If kept in water for a few days it gradually diminishes in bulk and becomes converted into a turbid, slimy solution, which is not capable of forming dough when mixed with starch. The convertibility of flour into dough, by the addition of water, depends upon the peculiar power which fresh gluten possesses of combining with water, and of forming with it a soft substance which does not yield its water to dry bodies which are placed in contact with it. Gluten, however, is a very hygroscopic substance; and when flour is kept exposed to the air for some time, it gradually absorbs moisture; in consequence of which the gluten slowly loses its tenacity, and undergoes a change similar to that which it experiences when placed in water. This change in the qualities of the gluten occurs more rapidly in rye flour than in wheat flour.

It has been ascertained by Liebig, that flour in which the gluten has undergone this partial change, may have its original qualities restored by the substitution of lime water for common water in the preparation of bread: 100 parts of flour are to be mixed with 26 or 27 parts of saturated lime water, and a sufficiency of ordinary water must be added to furnish dough of the proper consistence. A given weight of flour, when treated with lime water, was found to yield 5 or 6 per cent. more bread than when made in the ordinary way, and the bread so obtained is stated to be more palatable than common bread.

It is to be hoped that this simple method will supersede the employment of alum, which is commonly resorted to by English bakers, to whiten the bread and to improve the tenacity of the dough of inferior flour. Even sulphate of copper, a still more deleterious ingredient, which in minute quantity exerts a similar effect upon the dough, has been employed in Belgium and elsewhere, for improving the appearance and sponginess of the loaf. No satisfactory explanation has been afforded of the manner in which these salts act. In the case of sulphate of copper, a single grain in a 4lb. loaf has been found to produce a very marked alteration in the appearance of the bread (Kuhlmann, Poggendorff, *Annal.* xxi. 447). Fortunately, the addition of this poisonous salt can be detected in very minute quantities, by acidulating the crumb of the loaf and then moistening it with ferrocyanide of potassium, when the brown colour, characteristic of copper, is produced. If the bread be incinerated, the ash may be examined for copper in the usual method.

New and Stale Bread.—Newly baked bread exhibits a well-known elastic appearance, and possesses a certain degree of moisture, which renders it more palatable to most persons than bread which has been kept for a day or two, and has become firmer and drier in appearance, and which is commonly said to have become *stale*. It is very generally supposed that this change in properties in bread which has been kept for a few days, is owing to the loss of water by keeping. This, however, is not the case. The crumb of newly baked bread when cold, contains about 45 per cent. of water, and stale bread contains almost exactly the same proportion. The difference in properties between the two depends simply upon difference in molecular arrangement. Boussingault (*Ann. de Chimie,* III., xxxvi. 492) found that a loaf which had been kept for six days, though it had become very stale, had not lost more than 1 per cent. of its weight when new. This same loaf was then placed in the oven for an hour, and at the end of that time it had acquired all the properties and appearance of new bread, although during the second baking it lost 3½ per cent. of water. By enclosing a portion of bread in a tight case, to prevent loss of water by evaporation, the same piece of bread was restored to the condition of new bread, and then allowed to become stale many times in succession: a heat of about 130° was found to be sufficient to reconvert stale into new bread. Every person who has seen a thick slice of stale bread toasted, may have satisfied himself that the crumb has during this operation been converted into the same condition as that of new bread.

(*c*) *Lactic Fermentation.*

(959) It has already been mentioned, that sugar of milk does not undergo the vinous fermentation under ordinary circumstances. Milk, if it be kept in a warm temperature, may, notwithstanding, be converted into a spirituous liquor, which is in common use among the Tartars, who prepare it from mares' milk. Fruit sugar appears to be first formed by the action of the azotised constituents of milk upon the lactose, and the liquid

is then susceptible of the vinous fermentation. More commonly, however, sugar of milk, when allowed to ferment, yields a product of a very different nature; *lactic* acid being formed, as may be seen in the common case of milk turning sour in warm weather. This acid, in its hydrated form ($2\ HO, C_{12}H_{10}O_{10}$), has the same ultimate composition as sugar of milk; its oxygen and hydrogen being in the proportion to form water: but the arrangement of its particles is less complicated than that of sugar of milk; and its formation furnishes a good instance of the reduction of a complex body into one of a simpler constitution, by the process of fermentation. In this case, the casein or curd of the milk which is the basis of ordinary cheese, acts as the ferment. Casein is rendered insoluble by the presence of acids, and therefore it becomes separated in the form of insoluble flocculi, as soon as the milk turns sour. When all the curd has been thus rendered insoluble, the conversion of lactose into acid takes place very slowly, but if the acid be neutralized by carbonate of soda, the curd is redissolved, and the fermentation or transformation is renewed in its former vigour. No extrication of gas nor absorption of oxygen occurs during the process; the only perceptible change being the gradual disappearance of sugar of milk and the production of this peculiar acid, attended with the evolution of a peculiar offensive odour arising from the decay of the casein which accompanies the transformation. According to the observations of Boutron and Fremy, other animal matters undergoing decomposition are likewise capable of effecting the same transformation: moistened bladder, after exposure to the air for a certain time, and muscular and albuminous tissues, at a particular stage of their decomposition, possess the same property. But when the decomposition of the animal tissue has advanced beyond this particular stage, different products are obtained: fermentations or transformations are effected it is true, but the results of these changes are quite different, inasmuch as actions of a nature different from those required for producing lactic acid, are taking place in the body operating as a ferment. Not only sugar of milk, but starch, dextrin, cane sugar, and gum pass readily into lactic acid under the influence of casein and the other ferments already mentioned.

(*d*) *Viscous Fermentation.*

(960) Under certain circumstances, sugar becomes transformed into a mucilaginous substance, unattended by any evolution of gas;

the liquid loses its sweet taste, and acquires a *ropy* consistence, as is sometimes observed when sweet wines are kept for a time. This mucilaginous substance is insoluble in alcohol, and yields a precipitate with subacetate of lead, but it differs from ordinary gum in not yielding mucic acid when oxidized by nitric acid. A solution of tannic acid produces a precipitate when added to such a liquid, and checks the progress of the fermentation. This circumstance explains the observation, that red wines which contain a good deal of astringent matter derived from the husk and stalks of the grape, are not liable to become ropy. The tendency of a sweet liquid to become ropy is also arrested by the presence of sulphurous acid or of alum in small quantities; the alum causes the precipitation of the ferment in an insoluble form.

It has been found that various substances, such as boiled yeast, or the water in which flour or rice has been steeped, speedily cause sugar to undergo this transformation; and the sweet juice of the beet root, owing to the presence of an analogous substance, if left in a warm place for a few days, spontaneously passes into the viscous state. A quantity of mannite is usually formed at the same time in these cases.

CHAPTER III.

THE ALCOHOLS AND ETHERS.

§ I. The Alcohols.

(961) *General Characters of the Alcohols.*—The term alcohol was originally applied specifically to the volatile inflammable spirituous liquid, which is the characteristic product of the fermentation of sugar; but it has since been made generic, and is now extended to a class of bodies which possess chemical qualities analogous to those of wine alcohol, and which are homologues of that substance. Indeed, this class of compounds has already afforded us some striking illustrations of the existence of homologous groups (914).

The following is a list of the bodies at present known, which belong to the class of substances homologous with vinic alcohol; but there can be no doubt that as science progresses this list will be extended, and that ultimately an alcohol will be found corresponding to each term of the series of the volatile acids represented by the general formula, HO, $(C_nH_{n-1})\ O_3$:—

Alcohols.	Formula.	Specific Gravity		Boiling point. ° F.
	$(C_nH_{n+2}O_2)$ or $(C_nH_{n+1}O, HO)$	Liquid.	Vapour.	
1. Wood spirit, or methylic alcohol	$C_2\ H_4\ O_2$ or $C_2\ H_3\ O, HO$	0·798	1·12	149·9
2. Spirit of wine, or ethylic	$C_4\ H_6\ O_2$ „ $C_4\ H_5\ O, HO$	0·7938	1·6133	173
3. Tritylic, or propylic	$C_6\ H_8\ O_2$ „ $C_6\ H_7\ O, HO$		2·02	206
4. Tetrylic, or butylic	$C_8\ H_{10}O_2$ „ $C_8\ H_9\ O, HO$			233
5. Fousel oil, or amylic	$C_{10}H_{12}O_2$ „ $C_{10}H_{11}O, HO$	0·8184	3·147	269·8
6. Hexylic, or caproic	$C_{12}H_{14}O_2$ „ $C_{12}H_{13}O, HO$	0·833*	3·53	299-309
8. Octylic, or caprylic	$C_{16}H_{18}O_2$ „ $C_{16}H_{17}O, HO$	0·823	4·5	356
12. Lauric alcohol	$C_{24}H_{26}O_2$ „ $C_{24}H_{25}O, HO$			
16. Ethal, or cetylic	$C_{32}H_{34}O_2$ „ $C_{32}H_{33}O, HO$			
27. Ceroten, or cerylic	$C_{54}H_{56}O_2$ „ $C_{54}H_{55}O, HO$			
30. Melissin, or melissic	$C_{60}H_{62}O_2$ „ $C_{60}H_{61}O, HO$			

* At 32° F.

These substances, it will be seen, each contain 2 equivalents of oxygen, combined with quantities of carbon and hydrogen in which the number of equivalents of hydrogen always exceeds by two, the number of equivalents of carbon; an *even* number of equivalents of carbon being always present. The alcohols may all be regarded as compound oxides of hydrogen and of a peculiar hydrocarbon of which the general formula is C_nH_{n+1}. The general formula of an alcohol, therefore, may be represented as $C_nH_{n+2}O_2$, or (C_nH_{n+1}) O, HO, in which *n* represents an even number of equivalents of carbon. The alcohols by imperfect oxidation furnish *aldehyds;* and these bodies by the further absorption of oxygen yield *acids;* the latter in their hydrated form contain the same number of equivalents of carbon as the alcohol from which they were procured, but 2 equivalents less of hydrogen, and 2 equivalents more of oxygen, than the alcohol (*vide* table, page 33). The alcohols are further characterized by yielding, when treated with sulphuric acid and other dehydrating compounds, a class of substances termed *ethers*, which admit of being regarded as alcohols, minus 1 equivalent of water, though, as will hereafter be explained (986), there is reason to believe that this does not truly represent the mode of their formation.

(962) Alcohol; *Ethylic or Vinic Alcohol, Spirit of Wine:* $(C_4H_6O_2)$, *Eq.* 46, *Sp. gr. of liquid at* 60°, 0·7938; *of vapour*

1·6133.—Alcohol is a colourless volatile inflammable liquid, of an agreeable well-known spirituous odour, and an acrid burning taste. When pure it has a specific gravity of 0·815 at 32°. It boils at 173°, and has never been frozen, though at a temperature of — 166° F. it becomes viscid (Faraday). When taken in small quantities in a diluted form it furnishes a useful and well-known stimulant, forming the basis of all fermented liquors. In large quantities it produces intoxication, and acts as a powerful narcotic poison, frequently occasioning fatal results when taken in a concentrated state and in excess.

Alcohol furnishes a cleanly and valuable fuel to the chemist; it emits a high temperature during its combustion, and deposits no soot upon cold bodies which are introduced into its flame. When burned in air it emits but little light, and is wholly converted into carbonic acid and water: 4 volumes, or 1 equivalent of alcohol vapour, for complete combustion requires 3 times its bulk, or 12 equivalents of oxygen; $C_4H_6O_2 + 12\ O = 4\ CO_2 + 6\ HO$. When the vapour of alcohol is transmitted through red-hot tubes it is decomposed, carbon is deposited, and carburetted hydrogen, free hydrogen, and water, are produced.

When alcohol is exposed in its concentrated form to the atmosphere it attracts moisture, like sulphuric acid; and like this compound, when mixed with water it emits heat and contracts in bulk, though to a considerably less extent; the observed density of the mixture is therefore greater than its calculated mean density. According to Rudberg, the condensation is greatest when 53·739 measures of alcohol and 49·836 of water are mixed at 59°: these proportions correspond to 1 equivalent of alcohol and 6 equivalents of water; when cooled again to 59°, they occupy only 100 measures instead of 103·575, and have a sp. gr. of 0·927. From the importance of alcohol as an exciseable article, great labour has been bestowed upon the means for readily determining its percentage in spirituous liquors: the method in common use for distilled spirits consists in determining the specific gravity by means of a sensitive hydrometer, and tables have been constructed for showing the percentage of alcohol in mixtures of various densities. In these cases great attention must be paid to the temperature, since slight differences in this particular make a material variation in the density. The term *proof spirit*, in constant use among the excise, is defined by an Act of Parliament (58 George III.), to be "such as shall at the temperature of 51° F. weigh exactly twelve thirteenth parts of an equal measure of distilled water." It consists of water

50·76, alcohol 49·24 by weight, and indicates alcohol of sp. gr. 0·920 (Drinkwater 0·91984). The term derives its origin from the rude method of proof formerly in use, in which gunpowder was moistened with the spirit of wine to be tried, and the alcohol ignited; if it fired the powder it was said to be *over proof,* but if the spirit burned off and left the powder damp, it was considered *under proof;* the weakest spirit capable of thus firing powder had a sp. gr. of about 0·920.*

Alcohol is a solvent of great value to the chemist. It usually exerts but little chemical action upon the bodies which it dissolves, and owing to its volatility it is easily expelled by a gentle heat, leaving the substances which it previously held in solution in a pure state. Alcohol dissolves many of the gases freely; some of them, as, for instance, protoxide of nitrogen, carbonic acid, phosphuretted hydrogen and cyanogen, are dissolved by it more readily than by water. Iodine and bromine are also readily soluble in it, but the solutions gradually undergo decomposition in consequence of the reaction of iodine and bromine upon the alcohol. Absolute alcohol dissolves small quantities of phosphorus and of sulphur. The alkaline sulphides, as well as caustic potash and soda, are soluble in it to a very large extent; and ammoniacal gas is absorbed by it nearly as readily as by water; but it does not dissolve the carbonates of these alkalies. Alcoholic solutions of caustic potash and soda act powerfully as reducing agents upon many metallic solutions, such as those of platinum; they gradually absorb oxygen from the air, and become brown, owing to the formation of a resinoid substance.

Most of the deliquescent salts are soluble in alcohol, but the efflorescent salts, and those which are sparingly soluble in water, are not dissolved by it. Anhydrous alcohol combines with many anhydrous saline bodies in definite proportions, and forms with them crystallizable compounds, in which the alcohol, according to Graham, occupies the place of water of crystallization. The chlorides and the nitrates offer the best examples of the formation of these *alcoates.* The compound with chloride of calcium, $CaCl + 2\,(C_4H_6O_2)$, crystallizes readily; and analogous compounds may be obtained with the chlorides of zinc and of manganese, and with the nitrates of lime and of magnesia.

Alcohol likewise dissolves many organic bodies freely, such as the resins, the essential oils, the vegetable alkaloids, and many of the vegetable acids. It also dissolves more sparingly, sugar, and the soaps of potash, soda, and ammonia; but the fats and fixed oils, with the exception of castor oil, are dissolved by it in but small quantities.

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* In the Appendix two tables of the strength of alcohol at different specific gravities will be found.

A characteristic reaction of alcohol is its power of forming fulminate of silver, when 1 grain of silver is dissolved in 20 grains of nitric acid, and about 50 of alcohol are added; crystals of fulminate of silver are gradually deposited.

Preparation.—Alcohol may be obtained in a state of purity by subjecting to distillation any saccharine solution that has undergone fermentation; for being more volatile than water it passes over in the first part of the distillation, accompanied with more or less water. By repeated rectifications, or by a single operation in Coffey's still (175), it may be concentrated till it contains about 10 per cent. of water. Beyond this point the water adheres to it so strongly that it requires a different process for the complete separation of the last portions:—it is first rectified from charcoal, with a view of retaining all essential oils to which the peculiar odour and flavour of different spirits are mainly owing, and is then mixed with about half its weight of quicklime, and allowed to stand for three or four days: the lime gradually slakes and falls to powder in consequence of its conversion into a hydrate at the expense of the water in the alcohol; then, on applying heat by means of a bath of chloride of calcium, the pure spirit may be distilled off, the hydrate of lime retaining the water at temperatures far above 300° F. The alcohol thus obtained is anhydrous, or as it is often termed, ***absolute alcohol.***

Berthelot has recently pointed out a means of obtaining alcohol synthetically, by forming a solution of olefiant gas in oil of vitriol, then diluting the mixture and submitting it to distillation. Small quantities of dilute alcohol are thus obtained with facility (983). This process is the more interesting as it will possibly admit of application to the preparation of alcohols not hitherto isolated; most of the hydrocarbons which are homologous with olefiant gas are known in a separate form, though several of the alcohols are not: it appears probable, therefore, that by treating a solution of such hydrocarbons in oil of vitriol with water, and then distilling, the alcohols would be procured in small quantities without much difficulty.

(963) *Wines, Fermented Liquors, and Spirits.*—The various

Is a delicate test. [illegible] then [illegible] in [illegible] boiled and the alcohol added as [illegible] to the [illegible] which is [illegible] green —

kinds of spirits in use derive their names from accidental circumstances, often from the flavour which they possess. Thus, *gin* is spirit flavoured by distilling it with juniper berries; *peppermint* owes its aroma to the essential oil of the plant after which it is named; *whiskey* is spirit distilled from wort prepared from malt which has been dried over a peat fire, to which its peculiar flavour is due; *arrack* is a spirit distilled from fermented rice; and *rum*, a West Indian product from molasses; *brandy* is really the spirit of wine, being obtained from wines by distillation, and coloured more or less deeply with burnt sugar. In all these cases the characteristic flavour depends upon a small quantity of some volatile oil or compound ether which passes over with the spirit during the process of distillation. The varieties of spirits are very numerous, and those of fermented liquors which are used without subjecting them to distillation, are still greater. To this class belong all the different kinds of wine, which owe their peculiarities of flavour partly to the different flavour which the grapes possess in different climates, according as the saccharine, the aromatic, the acidulous, or the astringent principle of the fruit predominates, and also partly to the manner in which the liquid is prepared. When fermentation is allowed to proceed until all the sugar is transformed into spirit, a dry wine is produced; when checked before this term is reached, the result is a rich fruity wine; and when bottled whilst the fermentation is in full vigour, a brisk effervescent wine like champagne is the result. It is a common practice to add cane sugar to champagne before bottling. According to the experiments of Dr. Bence Jones, claret, Burgundy, and the wines of the Rhine and the Moselle, contain no sensible quantity of sugar; sherry yields from 1 to 5 per cent., port from 3 to 7 per cent., and Tokay as much as 17 per cent. of sugar. The ageing of wine and consequent change of flavour, depends partly upon the very gradual fermentation of sugar still retained in rich wines, and partly upon the slow separation of saline matter, principally in the form of bitartrate of potash, which becomes less soluble as the proportion of spirit increases, and is deposited, particularly from port wines, as a crust of tartar upon the sides of the bottle. An important part of the change of flavour appears also to be owing to the slow formation of minute quantities of fragrant and aromatic ethers which are gradually produced by the reaction of the vegetable acids upon the alcoholic portion of the wine.

Some wines instead of improving, become ropy by keeping.

This occurs only with sweet wines, and is due to a peculiar species of fermentation in which the sugar passes into the uncrystallizable form of mucilage (942, 960). Wines are usually 'white' or red, according as the husk of the grape is coloured or not, and according as the must has been allowed to ferment in contact with it or otherwise.

It is obvious that in wines and other fermented liquors which have not been submitted to distillation, all the soluble matter of the fruit is present in the beverage. Other saccharine juices, besides those of the grape, admit of being fermented, and thus a great variety of drinks may be produced. Beer and ale, for example, consist of an infusion of malt, flavoured by the aromatic bitter of the hop, and subsequently fermented. The different kinds of porter are similarly prepared, and owe their dark colour to the use of high-dried malt: *cider* is the fermented juice of the apple; *perry* is a similar liquor obtained from the pear; and nearly every fruit may be made to yield its own peculiar liqueur. Even savage nations evince a knowledge of this fact. The natives of the islands in the Pacific, when discovered by Cook, not only knew how to prepare an intoxicating liquor from the juice of the cocoa-nut, but they even rectified it by a rude process of distillation.

Since foreign matters are present in all fermented liquors, the specific gravity would, except in special cases, be no guide to the quantity of spirit contained in them.* A simple means of overcoming this difficulty was successfully practised by Mr. Brande:—carbonate of potash is soluble in water, but insoluble in alcohol: when perfectly dry carbonate of potash is poured into a mixture of alcohol and water, the salt becomes dissolved in the water, and the solution separates into two layers, the upper of which consists of alcohol of sp. gr. 0·825. By employing a graduated tube for the experiment, the volume of alcohol which is contained in any wine or liquor may be read off at once by inspection.

Dr. Christison submitted different wines to distillation, in order to determine their percentage of alcohol; he thus obtained a series of results, the most important of which are embodied in the following table. The numbers represent the weight of absolute alcohol contained in 100 parts of each variety of wine or fermented liquor:—

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* See "Report on Original Gravities" by M.M. Graham, Hofmann, and Redwood, (*Quart. Journ. Chem. Soc.* v. 229).

Port	from	14·97	to	17·10
Dry Lisbon		16·14		
Madeira	from	14·09	to	16·90
Sherry	„	13·98	„	16·17
Teneriffe		13·64		
Shiraz		12·95		
Malmsey		12·86		
Amontillado		12·63		
Claret	from	7·72	to	8·99
Hambacher		7·35		
Rudesheimer	from	6·90	to	8·40
Edinburgh ale	„	5·70	„	6·06
Best London porter		5·36		

(964) WOOD SPIRIT; or *Methylic Alcohol, Pyroxylic Spirit;* (C_2H_3O, HO). *Sp. gr. of liquid at* 32° 0·8179; *of vapour* 1·12.—Wood spirit has not as yet been procured by any process of fermentation; it is found amongst the volatile products obtained by the destructive distillation of wood at a high temperature in close vessels, accompanied by a large quantity of impure acetic acid, acetate of ammonia, acetate of methyl, tarry matter, and various hydrocarbons.

Purification.—In order to isolate the wood spirit, the crude products of the distillation are rectified by the heat of a water bath, and the product is distilled from quicklime, which retains the acetic acid, the water, and tarry matter. The wood naphtha of commerce is simply rectified from chalk; as thus prepared it is a mixture consisting chiefly of methylic alcohol and acetate of methyl, with certain oily hydrocarbons insoluble in water. In order to free it from these impurities, the commercial spirit may be saturated with chloride of calcium, which forms with pyroxylic spirit a compound not decomposable at the temperature of boiling water: the mixture is subjected to the heat of a steam-bath in a retort, and the volatile portions are thus expelled. The residue, which retains the wood spirit, is mixed with an equal weight of water, by which the spirit is displaced from its combination with the chloride; and on renewing the application of heat, pyroxylic spirit, mixed with a little water, passes over; a second rectification from quicklime furnishes it in a state of purity.

Properties.—Wood spirit is a limpid, inflammable, colourless liquid, of a penetrating empyreumatic odour, and a disagreeable burning taste. It has a sp. gr. of 0·798 at 68°, and boils at 149·9 (Kopp). It is soluble in water, alcohol, and ether, in all proportions. It is very inflammable, and burns with a pale flame, furnishing carbonic acid and water. When pure it does not reduce the subnitrate of mercury if mixed with its solution. Pyroxylic spirit mixes readily with the essential oils, and dissolves many fatty bodies and resins with facility. Its principal application in the arts, as crude wood naphtha, is founded upon its power of dissolving the resins, which, when thus dissolved, are employed as varnishes. A solution of shellac, and other resins in wood naphtha, is extensively used for stiffening the basis of silk hats. The hydrates of the alkalies are soluble in wood spirit, but they immediately colour it brown. Dr. Ure proposes to use this reaction as a means of discovering small quantities of pyroxylic spirit when mixed with alcohol; since alcohol is not thus altered in colour until after a considerable lapse of time.

It has already been mentioned that when alcohol is submitted to a gradual and incomplete oxidation, one of the products of the operation is aldehyd (971), which passes, by further oxidation, into acetic acid. Now, wood spirit may in like manner be subjected to partial oxidation, under the influence of finely divided platinum; and, though the different stages of the process have been less satisfactorily investigated than those which occur with ordinary alcohol, it appears that an intermediate substance is formed, which, like aldehyd, has the power of reducing the salts of silver; and finally, a strong solution of formic acid is produced. This acid stands in the same relation to the methylic series that the acetic does to the ethylic series:—

$$\overbrace{C_4H_5O,\ HO}^{\text{Alcohol.}} + 4\ O = \overbrace{HO,\ C_4H_3O_3}^{\text{Acetic Acid.}} + 2\ HO$$

$$\overbrace{C_2H_3O,\ HO}^{\text{Wood Spirit.}} + 4\ O = \overbrace{HO,\ C_2H\,O_3}^{\text{Formic Acid.}} + 2\ HO$$

This method, however, is not an advantageous one for the preparation of formic acid, since it is difficult to prevent the oxidation from going a stage further, and converting the formic acid into carbonic acid and water;

$$HO,\ C_2HO_3 + O = 2\ HO + 2\ (CO_2)$$

(965) *Tritylic* (or *propylic*) *Alcohol* ($C_6H_7O,\ HO$); ***Sp. gr. of vapour*** 2·02.—Although, during the ordinary process of the fer-

mentation of fruit or grape sugar, the products are carbonic acid and ordinary (ethylic) alcohol, it usually happens that minute quantities of other homologous bodies are formed. This is particularly the case when masses of the husk of the grape, from which the juice has been expressed (technically termed the *marc* of the grape), are thrown aside, and allowed to ferment. The saccharine matter which they still retain undergoes decomposition, and when the fermented liquor furnished by them is submitted to distillation, a mixture of tritylic, tetrylic (butylic), amylic, and hexylic (caproic) alcohol is obtained.

These different modes of fermentation admit of explanation by means of the following equations, in which it is assumed that in addition to the separation of carbonic acid, a certain quantity of water is eliminated at the same time:—

$$
\begin{aligned}
\overset{\text{Sugar.}}{2\,(C_{12}H_{12}O_{12})} &= 8\,CO_2 + 2\,HO + \overbrace{\overbrace{C_4H_6O_2}^{\text{Ethylic.}} + 2\,\overbrace{(C_6H_8O_2)}^{\text{Tritylic.}}}^{\text{Alcohols.}} \\
2\,(C_{12}H_{12}O_{12}) &= 8\,CO_2 + 4\,HO + 2\,\overbrace{(C_8H_{10}O_2)}^{\text{Butylic.}} \\
2\,(C_{12}H_{12}O_{12}) &= 8\,CO_2 + 4\,HO + \overbrace{(C_6H_8O_2)}^{\text{Tritylic.}} + \overbrace{(C_{10}H_{12}O_2)}^{\text{Amylic.}} \\
2\,(C_{12}H_{12}O_{12}) &= 8\,CO_2 + 4\,HO + \overbrace{(C_4H_6O_2)}^{\text{Ethylic.}} + \overbrace{(C_{12}H_{14}O_2)}^{\text{Hexylic.}}
\end{aligned}
$$

Tritylic alcohol, the third term of the alcoholic series, is obtained only in small quantity from the fermented marc. It is a limpid, colourless liquid, lighter than water, with an agreeable fruity odour. It boils at about 206°. Although freely soluble in water, it does not mix with it in all proportions.

(966) *Tetrylic* (or *butylic*) *Alcohol* (C_8H_9O, HO). *Sp. gr. of liquid* 0·8032; *of vapour* 2·589.—Wurtz procured this fourth term of the alcohols during the rectification of fousel oil obtained from beet-root spirits; it is contained in that portion which boils below 266°. By fractional distillation this portion may be made to yield a liquid, the boiling point of which remains steady at 233°, and which is the desired alcohol. Tetrylic alcohol is a colourless liquid of high refracting power, lighter than water, and only partially soluble in water. It has an odour resembling that of fousel oil, but less oppressive. When heated with the hydrate of potash, it is readily converted into butyrate of potash, with evolution of hydrogen; and, when mixed with concentrated sulphuric acid, it forms *sulphotetrylic* acid (HO, C_8H_9O, S_2O_6) without difficulty.

(967) **Amylic Alcohol.** *Fousel Oil, Potato Spirit* ($C_{10}H_{11}O$, HO). *Sp. gr. of liquid (at 32°)* 0·827; *of vapour* 3·147.—This substance, which constitutes the fifth term of the alcohol series, is a frequent impurity in brandies distilled from fermented potatoes, barley, rye, and the marc of grapes, to which it communicates a peculiar offensive odour and taste. Since it is considerably less volatile than either alcohol or water, it accumulates in the last portions of the liquid when such brandies are submitted to distillation.

Amylic alcohol is a colourless, limpid liquid, which has a persistent, penetrating, and oppressive odour, and a burning taste. It is but sparingly soluble in water, though it may be mixed with alcohol, ether, and the essential oils, in all proportions. Its vapour is very irritating when respired; it burns with difficulty with a bluish flame. The specific gravity of fousel oil at 59° is 0·8184. It boils at 269°·8 (Kopp), and at about —4° congeals into crystalline plates. Amylic alcohol causes a left-handed rotation of the plane of polarization in a ray of polarized light, but the extent of this power varies greatly in different specimens.

Under the influence of spongy platinum, amylic alcohol gradually absorbs oxygen, whilst hydrogen is eliminated in the form of water, and valeric acid is produced; this acid bears the same relation to amylic alcohol that acetic acid does to ordinary alcohol:—

$$\overbrace{C_{10}H_{12}O_2}^{\text{Fousel Oil.}} + 4\ O = \overbrace{HO,\ C_{10}H_9O_3}^{\text{Valeric Acid.}} + 2\ HO$$

The action of nitric acid upon amylic alcohol varies with the degree of its concentration and the temperature of the mixture, as it may be made to yield nitrate of amyl, valeric acid, valerate of amyl, or valeric aldehyd. Hydrate of potash is freely soluble in fousel oil. If fousel oil be heated on a mixture of hydrate of potash and lime to 430°, valerate of potash is formed, whilst hydrogen is liberated:—

$$C_{10}H_{12}O_2 + KO,\ HO = KO,\ C_{10}H_9O_3 + 4\ H.$$

When treated with phosphoric acid, or with chloride of zinc, fousel oil yields hydrocarbons homologous with olefiant gas.

(968) *Hexylic,* or *Caproic Alcohol* ($C_{12}H_{14}O_2$). *Sp. gr. at* 32° 0·833; *of vapour* 3·53.—This compound has also been obtained from the fermented marc of the grape. It is a limpid, aromatic liquid, which is insoluble in water, and boils between 299° and 309°. It

yields caproate of potash, with disengagement of hydrogen, when heated with hydrate of potash; caproic acid standing in the same relation to hexylic alcohol that acetic acid does to ordinary alcohol.

The seventh member of the alcoholic group is not yet known.

(969) *Octylic*, or *Caprylic Alcohol* ($C_{16}H_{18}O_2$). *Sp. gr. of liquid* 0·823 at 62°; *of vapour* 4·5.—This substance occurs in small quantity in the fermented marc of the grape; but its most interesting and available source is castor oil (Bouis. *Ann. de Chimie* III. xliv. 100). Castor oil consists principally of the glycerin compound of a peculiar acid, *ricinolic acid* (1132), the formula for the latter in its hydrated state being ($HO, C_{36}H_{33}O_5$). This acid, when heated with an excess of hydrate of potash to about 480°, undergoes decomposition; sebate of potash being formed whilst octylic alcohol and hydrogen are liberated, as shown by the following equation:—

$$\overbrace{HO, C_{36}H_{33}O_5}^{\text{Ricinolic Acid.}} + 2\,(KO, HO) = 2\,\overbrace{KO, C_{20}H_{16}O_6}^{\text{Sebate Potash.}} + \overbrace{C_{16}H_{18}O_2}^{\text{Octylic Alcohol.}} + 2\,H.$$

In order to isolate the alcohol, the castor oil is saponified by means of potash or soda, and afterwards an excess of the hydrated alkali, amounting to about half the weight of the oil operated upon, is added. The mass is heated moderately in a retort. It froths up at first considerably; but the foam gradually subsides, and a fragrant oily liquid distils over, which collects in the receiver above the water by which it is accompanied. The residue in the retort may be employed for the preparation of sebacic acid (1179). This distilled oil, which usually amounts to from a fourth to a fifth of the weight of the oil operated upon, must be purified by repeated rectifications from hydrate of potash, until the residue no longer has a brown colour.

Octylic alcohol is a colourless liquid, of a powerful persistent aromatic odour: it leaves a greasy stain upon paper, is insoluble in water, but freely soluble in alcohol and ether, as well as in acetic acid. It dissolves fatty and resinous bodies with facility. It undergoes no change when exposed to the air. The boiling point of octylic alcohol is 356°. It burns with a white luminous flame. Sulphuric acid combines with the alcohol, and forms *sulphocaprylic*, or *sulphoctylic* acid, which yields crystallizable salts. M. Bouis has obtained a large number of compound and double ethers with this alcohol; some of them are very fragrant and aromatic.

The other alcohols will be alluded to in speaking of the fats (1134, 1135, 1175).

§ II. PRODUCTS OF THE GRADUAL OXIDATION OF THE ALCO

(970) *General Properties of the Aldehyds.*—It has al been mentioned that when alcohol is burned with free of air, the sole products are carbonic acid and water. If, ever, the combustion be effected at a lower temperature, with a limited supply of air, numerous other compound formed, and the vapours emitted have a peculiar irritating on the eyes and nose, due principally to the production remarkable body, named *aldehyd.* The alcohol, in fact, is in fectly burned, 2 equivalents of hydrogen are converted into by union with 2 equivalents of oxygen from the air, and ald (dehydrogenated alcohol) is obtained:—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} + O_2 = \overbrace{C_4H_4O_2}^{\text{Aldehyd.}} + 2\ HO$$

Similar compounds are furnished by the imperfect combusti the other alcohols. The following are the principal bodie this class which have been examined:—

		Specific Gravity.		Boiling poin °F.
		Liquid.	Gaseous.	
Formic Aldehyd? .	$C_2H_2O_2$			
Acetic Aldehyd . .	$C_4H_4O_2$	0·79	1·532	7
Propionic Aldehyd .	$C_6H_6O_2$	0·79	2·169	about 14
Butyric Aldehyd . .	$C_8H_8O_2$	0·80		about 15
Valeric Aldehyd . .	$C_{10}H_{10}O_2$	0·82	2·96	23
Caproic Aldehyd . .	$C_{12}H_{12}O_2$			
Œnanthylic Aldehyd	$C_{14}H_{14}O_2$	0·827	4·178	about 31
Rutic Aldehyd . .	$C_{20}H_{20}O_2$	0·837	5·83	44

The aldehyds are characterized by their remarkable tend to combine with oxygen, in consequence of which they abso by mere exposure to the air, and become acid. Each equivale aldehyd absorbs 2 equivalents of oxygen, and is converted into corresponding acid; for example:—

$$\overbrace{(C_4H_4O_2)}^{\text{Acetic Aldehyd.}} \quad + \quad 2\ O \quad = \quad \overbrace{HO,\ C_4H_3O_3}^{\text{Acetic Acid.}}$$

$$\overbrace{C_8H_8O_2}^{\text{Butyric Aldehyd.}} \quad + \quad 2\ O \quad = \quad \overbrace{HO,\ C_8H_7O_3}^{\text{Butyric Acid.}}$$

Most of the aldehyds combine with ammonia, and form wit compounds which are insoluble in ether. When mixed wi solution of potash, they form with the alkali a brown resi mass. Many of them when heated with a solution of nit of silver, to which a small quantity of ammonia has been added, decompose the salt of silver, and reduce the metal in the form of a mirror-like coating upon the inner surface of the vessel in which they are heated. Another remarkable property of the aldehyds is their power of forming with bisulphites of potash and soda crystalline compounds of stable character and sparing solubility (Bertagnini, *Liebig's Annal.* lxxxv. 179). These compounds contain the elements of one equivalent of bisulphite of the alkali, and one of the aldehyd, with or without water of crystallization, having the general formula, ($HO, KO, 2\,SO_2 + C_nH_nO_2 + x\,Aq$). Many essential oils, such as those of bitter almonds, cinnamon, cummin, and spiræa, form similar compounds. These bodies are probably the aldehyds of a different class of alcohols.

The theoretical composition of the aldehyds has been variously represented. Liebig proposed to regard acetic aldehyd as $(C_4H_3)O, HO$, or as the hydrated oxide of a peculiar radicle C_4H_3, termed *acetyl;* and a similar view would of course apply to the aldehyds since discovered: they may also be regarded as compounds in some measure analogous to hydrogen itself, acetic aldehyd being then represented by the formula $\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}$ in accordance with the hydrogen type $\left.\begin{matrix}H\\H\end{matrix}\right\}$. These views will be discussed more fully when the properties of acetic aldehyd are considered.

The aldehyds are unstable compounds, several of them passing into bodies which are isomeric with them, but which possess properties entirely different from the true and rapidly oxidizable aldehyds.

(971) ALDEHYD, *Acetic aldehyd* ($C_4H_4O_2$); *Sp. gr. of liquid at* 32°, 0·8009; *of vapour* 1·532.—Acetic aldehyd was the earliest discovered member of the group of aldehyds, and owing to its connexion with the process of acetification it is by far the most important of them.

Preparation.—Aldehyd may be formed by the gradual oxidation of alcohol in various ways: thus it is formed when the vapour of alcohol mixed with air is transmitted through a porcelain tube heated to low redness, or when alcohol is acted upon by dilute nitric or chromic acid: owing to the action of nitric acid upon the elements of alcohol, it is always present in nitrous ether: and it may also be procured by the dry distillation of lactic acid, or of lactate of copper. Another remarkable mode in which aldehyd may be obtained has been pointed out by Natanson: he finds that when chloride of acetylium (1069) is mixed with nitrite of silver and a little sulphuric acid, a copious evolution of nitrogen occurs, and aldehyd is formed abundantly;—

$$\overbrace{C_4H_3,\ H_3NCl}^{\text{Chloride of Acetylium.}} + NO_3 = \overbrace{C_4H_3O,\ HO}^{\text{Aldehyd.}} + 2\ N + HO + HCl.$$

Acetylium is itself derived from Dutch liquid by the action of ammonia upon it; whence it would appear that a close relationship exists between olefiant gas and aldehyd.

None of these reactions are employed for the preparation of aldehyd, since there are more convenient methods. One of these consists in placing three parts of bichromate of potash and three of alcohol in a retort, and allowing four parts of sulphuric acid to pass drop by drop into the mixture, the vapours being condensed in a proper refrigeratory.

Aldehyd is however usually procured by Liebig's method of distilling in a capacious retort, a mixture of 6 parts of sulphuric acid, 4 of alcohol (sp. gr. 0·850), 4 of water, and 6 of finely powdered black oxide of manganese. In this process the oxide of manganese is decomposed, sulphate of protoxide of manganese is formed, whilst the second equivalent of the oxygen of the oxide of manganese combines with the hydrogen of part of the alcohol, and aldehyd is formed and passes over. The product being very volatile must be condensed in vessels cooled with ice, and the process must be stopped when the distillate becomes acid. Since, however, it is in a very dilute and impure condition, it is to be rectified from an equal weight of chloride of calcium, in order to free it from alcohol and water. This operation is repeated twice, or even three times. The distilled liquid still retains alcohol, besides a small quantity of acetic ether, and a liquid termed acetal (973). For the purpose of obtaining it free from these impurities it is mingled with twice its bulk of anhydrous ether, and saturated with dry ammoniacal gas, while the liquid is artificially cooled: prismatic needles of snowy whiteness are thus formed; these crystals consist of a compound of aldehyd with ammonia ($NH_3,\ C_4H_4O_2$) which is insoluble in ether, though very soluble in water; they may be dried in the open air; they fuse at a heat a little below 212°, and at 212° may be sublimed unchanged. If heated in the open air they take fire, and burn with flame. After a time, even when kept in closed

$6\ MnO_2 . 6\ SO_3 . 4\ HO . 4\ C_4H_6O_2 = 6(MnO\ SO_3$ [illegible] $HO)\ 6\ HO,\ C_4H_6O_2 ,\ 4\ HO.$

vessels, the crystals become brown, and emit an odour like that of burned feathers. To obtain pure aldehyd from them, two parts of the crystals dissolved in two of water, are distilled with three of oil of vitriol diluted with four parts of water; the product is received in vessels surrounded with ice, and is finally rectified from chloride of calcium.

Properties.—Aldehyd is a volatile inflammable liquid, with a peculiar pungent irritating odour, which has a faint resemblance to that of apples. It boils at 70° F., and has a sp. gr. of 0·79 at 65°. It may be mixed in all proportions with alcohol, ether, and water. It has no acid reaction upon litmus paper, but it can scarcely be exposed to the air without absorbing oxygen, and it then forms an acid compound. Aldehyd yields with ammonia the peculiar crystalline compound already described, but when similarly treated with potash it gives a brown resinous mass: this is one of its most characteristic reactions. Another striking one is its power of reducing the oxide of silver, and of yielding, when boiled with solutions of the salts of this metal, a mirror-like coating of silver upon the sides of the tube in which the experiment is made: the solution should be rendered feebly alkaline by the addition of a few drops of a weak solution of ammonia. In this experiment a portion of the aldehyd is converted into *acetous* or *aldehydic* acid, at the expense of the oxygen derived from a portion of the oxide of silver which is thus reduced to the metallic state, and the newly formed aldehydic acid enters into combination with a portion of the undecomposed oxide of silver:—

$$\overbrace{C_4H_4O_2}^{\text{Aldehyd.}} + 2\,AgO = Ag + HO + \overbrace{AgO,\,C_4H_3O_2}^{\text{Aldehydate Silver.}};$$

the aldehydate of silver remains in solution (Liebig). The existence of aldehydic acid as a definite compound is however rather questionable.

Chlorine displaces a portion of the hydrogen of the aldehyd, converting it into chloral (1017);

$$\overbrace{C_4H_4O_2}^{\text{Aldehyd.}} + 6\,Cl = \overbrace{C_4HCl_3O_2}^{\text{Chloral.}} + 3\,HCl.$$

Aldehyd, when transmitted over a mixture of lime and hydrate of potash in a heated tube, first becomes brown, and is then decomposed with disengagement of hydrogen, leaving a white mass composed of acetate of potash:—

$$\overbrace{C_4H_4O_2}^{\text{Aldehyd.}} + KO,\,HO = \overbrace{KO,\,C_4H_3O_3}^{\text{Acetate of Potash.}} + 2\,H.$$

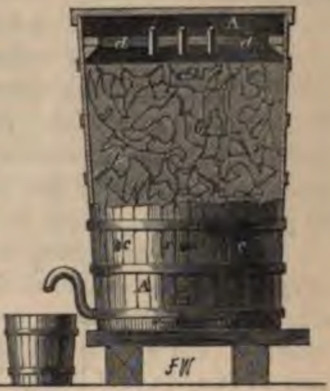
Potassium when placed in contact with aldehyd disengages hydrogen, and forms a soluble compound ($C_4H_3O_2K$) possessed of an alkaline reaction, which absorbs oxygen readily. This compound contains the elements of aldehyd, in which one equivalent of potassium has displaced one of hydrogen.

Aldehyd when kept has been known to undergo a remarkable spontaneous conversion into two new substances, each isomeric with it; one of these is a solid crystalline body, *metaldehyd*, which may be sublimed at 248°, before undergoing fusion: the other retains the liquid form and is termed *elaldehyd;* the latter may be mixed with water, alcohol, and ether, in all proportions; it boils at 201°, and freezes at 35·6°. The density of its vapour according to Fehling is 4·5157, which is three times that of aldehyd; elaldehyd appears therefore to have been formed by the condensation of the elements of three equivalents of aldehyd into one. A third isomeric body termed *paraldehyd*, which is liquid, and boils at 257°, is formed when aldehyd diluted with an equal bulk of water is exposed with a trace of sulphuric or nitric acid to a cold of 32°; crystals of metaldehyd are deposited, and paraldehyd remains in the liquid; the sp. gr. of its vapour is 4·583; its equivalent volume coinciding with that of elaldehyd.

(972) *Preparation of acetic acid.*—The principal interest, however, with which aldehyd is invested, arises from the facility with which it absorbs oxygen, and its consequent connexion with the process of acetification. When alcohol is exposed to the united influence of atmospheric air and finely divided platinum, partial oxidation occurs, and aldehyd is produced in abundance: and, owing to the readiness with which aldehyd absorbs oxygen, an attempt was made to carry the oxidation a step further, and thus to prepare acetic acid on a large scale by this method. The use of platinum, however, is now abandoned, but the manufacture of vinegar upon this principle is still extensively followed. In Germany, and in other countries where the legislature imposes no duty upon alcohol, dilute spirit mixed with a small quantity of infusion of malt is the ordinary material employed in the manufacture of vinegar. The mode of procedure is the following:—Large vats, of the form shown in A, A, fig. 334, provided with a loosely fitting lid, and furnished with apertures at top and bottom *c, c*, and *d, d*, for the free admission and egress of air, are filled with deal or beech shavings, first dried and then soaked in strong vinegar; these shavings rest upon a perforated shelf which is supported just above the level of the lower apertures, *c, c*. A mixture consisting

of 1 part of alcohol, sp. gr. 0·850, of 6 parts of water, and $\frac{1}{1000}$th of honey, yeast, or wort, is allowed to trickle slowly through the shavings, whilst the temperature is raised to about 80° F. The acetification does not proceed rapidly until the process has been in operation for some days. It is supposed that a peculiar kind of fungus or slimy vegetable mould which is gradually formed upon the shavings, and which is known under the name of *mother of vinegar*, acts somewhat in the manner of a ferment and accelerates the oxidation. It is remarkable that the presence of a very minute quantity of any empyreumatic or tarry matter is sufficient entirely to put a stop to the transformation. As the operation proceeds, the heat rises to about 100° or 105°; at which point it remains stationary. When the alcohol has been made to pass through the vat four or five times, its conversion into vinegar is usually complete. Well-burned charcoal purified from saline matters by hydrochloric acid, and then thoroughly washed, may be substituted for the shavings with good effect. In this operation a large surface is exposed to the air, aldehyd is formed, and it immediately absorbs oxygen from the atmosphere, being thus at once converted into common vinegar or acetic acid :—

FIG. 334.



$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} + 2\,O = \overbrace{C_4H_4O_2}^{\text{Aldehyd.}} + 2\,HO;\ \text{and}$$

$$\overbrace{C_4H_4O_2}^{\text{Aldehyd.}} \ + \ 2\,O \ = \ \overbrace{HO,\ C_4H_3O_3}^{\text{Acetic Acid.}}.$$

Pure dilute alcohol, however, does not absorb oxygen when exposed to the atmosphere; it requires the presence of some vegetable matter prone to decomposition to induce the oxidation; and it is for this reason that honey or sweet wort is added in the foregoing operation.

If the supply of air be insufficient, a large quantity of alcohol is wasted, owing to the formation of aldehyd, which from its great volatility, passes off in vapour before it has become oxidized and converted into acetic acid.

Different views have been taken of the nature of alde Liebig considered it as a hydrated oxide of a peculiar hydroca (C_4H_3) not hitherto isolated, but which he named *acetyl*, a supposed it to form an essential constituent of acetic acid. If be so, the connexion of aldehyd with acetic acid may be represented—

$HO, (C_4H_3) O =$ hydrated oxide of acetyl, or aldehyd.
$HO, (C_4H_3) O_2 =$ hydrated acetous or aldehydic acid.
$HO, (C_4H_3) O_3 =$ hydrated acetic acid.

These three compounds, therefore, would be looked upo hydrates of three successive oxides of the same radicle; a much strengthened by the fact that the last two compounds be procured in succession by oxidation of the lowest oxide.

Gerhardt, considering that the radicle of acetic acid con oxygen, represents this radicle as $C_4H_3O_2$, and he supposes tha other acids of the same series all contain homologous oxi radicles; the radicle of formic acid, for instance, being C_2 that of butyric acid being $C_8H_7O_2$, and so on. The aldehyd regarded by him as hydrides of these radicles which have a tend to become oxidized: both the hydrogen and the assumed ra of the acid becoming oxidized simultaneously. These rela may be thus indicated—

Radicle.	Aldehyd.	Hydrated Acid.
Formic . C_2HO_2	C_2HO_2, H	HO, C_2HO_2, O
Acetic . . $C_4H_3O_2$	$C_4H_3O_2, H$	$HO, C_4H_3O_2, O$
Butyric . $C_8H_7O_2$	$C_8H_7O_2, H$	$HO, C_8H_7O_2, O$
Valeric . $C_{10}H_9O_2$	$C_{10}H_9O_2, H$	$HO, C_{10}H_9O_2, O$
&c.	&c.	&c.

Considerable probability is given to this view by the exist of many compounds in which the two equivalents of ox assumed to exist in the radicle are preserved in the compo derived from it; but the nature of the aldehyds and their logues, the *ketones* (1069), is still unsettled. Gerhardt does admit the existence of acetous acid ($HO, C_4H_3O_2$), or of bo homologous with it.

The tendency of aldehyd to rapid oxidation will affor explanation of the fact that platinum black always furnishe acid product by its reaction on alcohol. Aldehyd is first for but it immediately undergoes partial oxidation, by which i converted into a mixture of aldehydic and acetic acids. F process somewhat similar, weak fermented, but not distil liquors frequently become sour when exposed to the air in warm weather, a change which forms the basis of the usual method of preparing white wine and malt vinegars; the mucilaginous and albuminous matters present in the wort or beer absorb oxygen, and induce a similar process of oxidation in the alcohol, in consequence of which acetic acid is formed. The more completely fermentation has taken place, the less likely is vinegar to be formed; since, during the fermentation, the azotised and other matters necessary to further the oxidation of the alcoholic portion are gradually destroyed. If much albuminous matter remain in solution in the vinegar after it is formed, the acid is itself liable to undergo a further change; a peculiar mould or fungus appears upon the surface of the liquid, and the acid is slowly decomposed; the cellulose or ligneous tissue of the fungus being formed at the expense of the constituents of the acetic acid;

$$9\ (\overbrace{\mathrm{HO,\ C_4H_3O_3}}^{\text{Acetic Acid.}}) = \overbrace{\mathrm{C_{36}H_{30}O_{30}}}^{\text{Cellulose.}} + 6\ \mathrm{HO}.$$

The formation of aldehyd appears always to precede the production of vinegar, just as the transformation of cane into grape sugar precedes the vinous fermentation. Acetification, however, is not a true process of fermentation; it is rather one of gradual oxidation, and differs from fermentation in the important fact that the absorption of oxygen is necessary during the whole course of the operation; and if the supply of oxygen be arrested, the further production of acid is immediately stopped.

(973) *Acetal* ($C_{12}H_{14}O_4 = 2\ C_4H_5O,\ C_4H_4O_2$), *Sp. gr. of liquid* 0·825; *of vapour* 4·24.—This compound was discovered by Döbereiner among the products furnished by the slow oxidation of alcohol under the influence of finely divided platinum. A number of watch glasses containing platinum black (823) are placed in a jar, into the lower part of which a few ounces of alcohol have been introduced: the jar is covered with a glass plate, and left for a few days in a temperature of about 70°, taking care to renew the air in the jar from time to time. The alcohol rises in vapour and undergoes slow oxidation, the liquid becomes condensed upon the sides of the jar, and the products collect at the bottom. The viscid liquid thus obtained consists of a mixture of alcohol, aldehyd, acetic ether, and acetal. It is first rectified from carbonate of potash; and on adding chloride of calcium to the distillate so long as any of the salt is dissolved, a layer of acetal is separated, and rises to the surface: this is removed by means of a pipette, after which

the cautious addition of water to the solution of chloride of c cium causes the separation of an additional quantity of the sar liquid. It is purified by rectifying it from chloride of calciu Acetal forms a colourless liquid, of an agreeable characteristic odo and a flavour resembling that of hazel nuts. It boils at 221°, a is soluble in about 6 parts of water, but its solubility diminish as the temperature rises: it is soluble in all proportions in alcoh and ether. Aqueous solutions of the alkalies, if excluded from t air, do not decompose acetal. (Stas. *Ann. de Chimie,* III., xix. 14 Oxidizing agents transform it first into aldehyd, and then into ace acid. Acetal may be regarded as a combination of aldehyd w ether; 3 equivalents of alcohol concurring to its production:—

$$3\,(\overbrace{C_4H_6O_2}^{\text{Alcohol.}}) + O_2 = \overbrace{2\,C_4H_5O,\ C_4H_4O_2}^{\text{Acetal.}} + 4\,HO.$$

(974) *Propionic Aldehyd* ($C_6H_6O_2$); *Sp. gr. of liquid* 0·79; *vapour* 2·169.—The aldehyds which still remain to be noticed, comparatively unimportant. *Formic aldehyd* has not hitherto b satisfactorily isolated, but *methylal,* a body homologous with ace is contained amongst the products of the gradual oxidation of w spirit by means of peroxide of manganese and sulphuric acid.

Propionic aldehyd was found by Guckelberger amongst products furnished by distilling albuminous substances with a m ture of sulphuric acid and peroxide of manganese (Liebig's *Anna* lxiv. 42). It passes over mixed with acetic and butyric aldeh as well as with the oil of bitter almonds (hydride of benzo Propionic aldehyd is a limpid liquid of an ethereal odour; it soluble in water, alcohol, and ether, in all proportions. It b between 131° and 149°, and becomes slowly acid when exposed the air, yielding propionic acid.

(975) *Butyric Aldehyd* ($C_8H_8O_2$), *Sp. gr. liquid* 0·8, is obtai during the same process as the foregoing compound. It is a colo less liquid which is very sparingly soluble in water, but is fre dissolved by alcohol and ether. It has an ethereal pungent od and a burning taste, and becomes rapidly converted into buty acid by exposure to the air. It forms with ammonia the crystall compound characteristic of the aldehyds, and when heated wit solution of nitrate of silver, gives a brilliant mirror of redu metal. It boils between 154° and 163°.

An isomeric compound, termed *butyral* by Chancel, obtained by the distillation of dry butyrate of lime. It boils 203°, yielding a vapour of sp. gr. 2·61; and when exposed to the rapidly becomes converted into butyric acid. It, however, yields no compound with ammonia, and does not reduce the nitrate of silver.

(976) *Valeric Aldehyd* ($C_{10}H_{10}O_2$), *Sp. gr. of liquid* 0·82, *of vapour* 2·96.—This compound may be obtained in various ways. One of the best consists in oxidizing fousel oil by means of a mixture of sulphuric acid and bichromate of potash :—37 parts of bichromate of potash dissolved in warm water and placed in a retort, are to be gradually mixed with 49 parts of oil of vitriol, diluted with an equal bulk of water; 33 parts of fousel oil are then to be carefully added; the aldehyd distils over without the necessity for applying heat. If the distillate be mixed with a saturated solution of bisulphite of soda, the compound of bisulphite of soda and valeric aldehyd crystallizes readily, and may be purified by recrystallization from alcohol. If these crystals be mixed with a solution of carbonate of potash, and distilled, valeric aldehyd passes over, and may be dried over chloride of calcium. This aldehyd is a highly mobile, limpid, colourless liquid, with a burning taste and a pungent, penetrating odour. It boils at 230°, emitting an inflammable vapour. It is insoluble in water, but soluble in alcohol and ether. By oxidation it is rapidly converted into valeric acid.

(977) *Œnanthylic Aldehyd; Œnanthol* ($C_{14}H_{14}O_2$), *Sp. gr. of liquid* 0·8271 *at* 63°; *of vapour* 4·17.—This aldehyd is furnished by the destructive distillation of castor oil. In order to purify the crude distillate, it is agitated with baryta water, which retains the volatile acids; the oil, which rises to the surface on standing, is submitted to distillation, and is then dried by digestion on chloride of calcium. Water dissolves it sparingly; the boiling point of the oil is about 312°. It rapidly absorbs oxygen from the air, and becomes converted into œnanthylic acid.

(978) *Rutic or Capric Aldehyd* ($C_{20}H_{20}O_2$), *Sp. gr. of liquid at* 64° 0·837; *of vapour* 5·83.—This substance is the chief constituent of the essential oil of rue. It may be purified by distillation. This oil has a somewhat viscid consistence; it possesses the strong disagreeable odour of the plant, and an acrid, bitterish, somewhat aromatic taste. It boils at about 446°, and at a temperature of about 29° or 30° concretes into brilliant transparent laminæ. Nitric acid acts rapidly upon oil of rue, and furnishes different products according to the degree of concentration of the acid; by the prolonged action of the concentrated acid, pelargonic acid ($HO, C_{18}H_{17}O_3$), and the lower homologues of the groups of acids are obtained; by moderating the action of the nitric acid, rutic acid (HO,

$C_{20}H_{19}O_3$) is procured. Essence of rue does not absorb oxygen very rapidly, nor is it easily converted when heated with hydrate of potash into the rutate of this base; but it combines readily with the alkaline bisulphites, and forms with them crystallizable compounds which correspond with those formed with the other aldehyds.

The acids produced by the oxidation of the alcohols and aldehyds would naturally be taken into consideration at this point, but it will be more convenient to defer the description of these compounds until the fats have been examined (1152, *et seq.*).

§ III. ACTION OF THE ACIDS UPON THE ALCOHOLS.

(979) WHEN a hydrated acid is mixed with one of the alcohols, several cases may arise, dependent on the nature of the acid, the proportions in which it is added, and the temperature applied to the mixture.

1st. If a polybasic acid which has a strong affinity for water, such as the sulphuric, the phosphoric, or the arsenic, be added to one of the alcohols, the elements of the acid and of the alcohol enter into combination and form a new compound acid; a *vinic acid* being produced, in quantity varying with the temperature and relative proportions of the acid and the alcohol.

2nd. If such a mixture be submitted to distillation, the alcohol is decomposed, and a quantity of ether is formed and volatilized; whilst the residue in the retort is capable of effecting the etherification of fresh portions of alcohol.

3rd. If the proportion of acid to the alcohol exceed a certain amount, or if the temperature at which the distillation is effected rise beyond a certain point, the decomposition proceeds further, and a number of hydrocarbons homologous with olefiant gas are formed; whilst at still higher temperatures the acid originally used begins to undergo decomposition, and the products are still more complicated.

4th. When an organic acid is submitted to distillation with one of the alcohols, a double decomposition occurs, and a compound ether is produced, whilst the elements of water are separated; thus,

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2}^{\text{Acetic Acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} = \overbrace{\left.\begin{matrix}C_4H_3O_2\\C_4H_5\end{matrix}\right\}O_2}^{\text{Acetic Ether.}} + \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}}.$$

It is generally found advisable in such cases to use a salt of the organic acid, and after this salt has been mixed with a due proportion of alcohol, to decompose it by the addition of sulphuric acid.

5th. If a hydracid, such as the hydrochloric, hydrobromic, or hydriodic be made to act upon an alcohol, double decomposition occurs, and an ether is formed by the substitution of the radicle of the alcohol for the hydrogen of the hydracid; thus, when hydrochloric acid acts upon alcohol, water and hydrochloric ether are the result:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} + \overbrace{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}^{\text{Hydrochloric Acid.}} = \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}} + \overbrace{\left.\begin{matrix}C_4H_5\\Cl\end{matrix}\right\}}^{\text{Hydrochloric Ether.}}$$

The Vinic Acids.

(980) When a mixture of concentrated sulphuric acid with any of the alcohols is heated to about 212°, a portion of the two compounds enters into combination, and the result is the formation of a new coupled acid in which the elements of 1 equivalent of the alcohol and 2 equivalents of sulphuric acid are present. In these compounds the existence of sulphuric acid is no longer indicated by the formation of an insoluble sulphate of baryta on the addition of chloride of barium; the baryta salt of these acids being readily soluble in water.

The following may be taken as examples of a few of the compound acids thus obtained:—

	Hydrates.	Potash Salts.
Sulphomethylic . . .	$HO, C_2 H_3 O, 2 SO_3$	$(KO, C_2 H_3 O, 2 SO_3 + Aq)$
Sulphethylic, or sulpho-vinic	$HO, C_4 H_5 O, 2 SO_3$	$(KO, C_4 H_5 O, 2 SO_3)$
Sulphotritylic (propylic)	$HO, C_6 H_7 O, 2 SO_3$	$(KO, C_6 H_7 O, 2 SO_3)$
Sulphotetrylic (butylic) .	$HO, C_8 H_9 O, 2 SO_3$	$(KO, C_8 H_9 O, 2 SO_3)$
Sulphamylic	$HO, C_{10} H_{11} O, 2 SO_3$	$(KO, C_{10} H_{11} O, 2 SO_3 + Aq)$
&c.	&c.	&c.

These acids form crystallizable salts with potash, as well as with lime, baryta, and many other bases; but the salts thus formed are unstable, and sometimes undergo spontaneous decomposition; these compounds have a peculiar pearly lustre. It is important to remark, that although the acid contains the elements of two equivalents of sulphuric acid, the salts are monobasic, and contain only one equivalent of metallic oxide, as may be seen by inspecting the column headed 'potash salts.'

The hydrates of these sulpho-acids are more unstable than their metallic salts; they cannot be distilled without undergoing decomposition, and they then break up into the ether corresponding to the alcohol which furnished them, and sulphuric acid. If diluted with water and heated, the solution becomes rapidly converted into a mixture of dilute sulphuric acid, and the alcohol from which the compound was originally obtained: for instance,

$$\overbrace{HO,\ C_4H_5O,\ 2\ SO_3}^{\text{Sulphethylic Acid.}} + 2\ HO, = \overbrace{HO,\ C_4H_5O}^{\text{Alcohol.}} + 2\ (HO,\ SO_3).$$

The most interesting of these acids is the sulphethylic, and it is necessary to examine its properties on account of the important part which it has occupied in the theory of etherification.

(981) *Sulphethylic, or Sulphovinic Acid* ($C_4H_6O_2$, $2\ SO_3 = HO$, C_4H_5O, $2\ SO_3$).—When alcohol is mixed with an equal measure of oil of vitriol, great heat is evolved, and the two bodies enter partially into combination.* The sulphuric acid thus combined with the elements of alcohol, loses half its saturating power, and the compound acid forms with baryta, with lime, and with oxide of lead, salts which are soluble in water. By adding sulphuric acid gradually to a solution of the baryta salt, until no further precipitate of sulphate of baryta is produced, the acid is set at liberty in a state of purity. It was originally called the *sulphovinic acid*, but the term *sulphethylic*, by which it is now frequently described, is better, as it forms one of a numerous class of analogous acids. Sulphethylic acid may also be formed by gradually adding ether, perfectly free from alcohol, to concentrated sulphuric acid; the temperature rises rapidly, but must not be allowed to exceed 250°: on diluting the mixture with water it will be found that nearly the whole of the ether has been converted into sulphethylic acid. It is worthy of notice in connexion with the theory of etherification (990), that when alcohol is mixed with sulphuric acid, diluted till it contains 4 equivalents of water (HO, SO_3, $3\ Aq$), no sulphethylic acid is formed at ordinary temperatures, but this acid is produced if the temperature be raised to 212°.

The hydrated acid is very unstable. If diluted with water and distilled, alcohol passes over, and nothing but sulphuric acid is left in the retort; but it may be concentrated in vacuo, when it forms a colourless syrupy liquid, of a sharp acid taste, not miscible with ether. It gradually undergoes spontaneous decomposition. When heated in the presence of an excess of alcohol, it experiences a remarkable decomposition, to which it will be necessary to give particular attention (990), owing to its being attended with the formation of ether in large quantity.

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* The alcohol is never wholly converted into the new acid, for even if anhydrous alcohol be mixed in the above proportions with monohydrated sulphuric acid, not more than half the alcohol becomes converted into the vinic acid, since, in the act of combination, a portion of water is displaced from the oil of vitriol; and on applying a heat of 212°, diluted alcohol gradually passes over, though the liquid does not boil at this temperature.

The sulphethylates are all freely soluble in water; many of them are likewise dissolved by alcohol; most of these salts crystallize with facility in pearly scales which have a greasy feel. When subjected to dry distillation, they yield olefiant gas, heavy oil of wine, and sulphurous and carbonic acids, leaving a residue of sulphate of the base, mixed with charcoal. If distilled with hydrate of potash they yield alcohol. When in solution they are decomposed at a boiling temperature, the solution, if neutral, becoming acid during the ebullition; but this change is prevented in the case of the sulphethylate of potash and soda, by the addition of a few drops of a solution of the hydrates of these alkalies.

Sulphethylate of potash is anhydrous and somewhat deliquescent, but insoluble in alcohol or ether. It crystallizes readily in large tables. *Sulphethylate of baryta* crystallizes with 2 equivalents of water in rhombic prisms, which are soluble in water and in alcohol. *Sulphethylate of lime* ($CaO, HO, C_4H_5O, S_2O_6, 2\ Aq$) crystallizes in thin six-sided tables, very soluble in water but not in ether. It sometimes undergoes spontaneous decomposition. The neutral *sulphethylate of lead* ($PbO, C_4H_5O, S_2O_6, 2\ Aq$) forms colourless tables, which are soluble in water and in alcohol; they are liable to spontaneous decomposition. If digested upon an excess of oxide of lead, a soluble uncrystallizable subsalt, with 2 equivalents of base, is formed.

Acids isomeric with the Sulphethylic.—Besides sulphethylic (sulphovinic) acid, there appear to be three other isomeric sulpho-acids formed by the action of oil of vitriol upon alcohol, viz.: the isethionic, parathionic, and althionic acids.

(982) *Isethionic Acid* ($HO, C_4H_5S_2O_7$). — This acid is at once distinguished from the sulphethylic by the greater stability of its salts, which may generally be heated to 400°, without experiencing decomposition. Isethionic acid is formed readily by boiling a strong solution of ethionic acid (984) for some time. On neutralizing the solution by means of carbonate of baryta, the isethionate of baryta ($BaO, C_4H_5S_2O_7$) is obtained, and may

be procured in hexagonal tables which may be heated to 608°, when they fuse without undergoing decomposition. By a stronger heat they are decomposed, and blacken, swelling up very considerably. *Isethionate of potash* crystallizes in anhydrous rhomboidal prisms, which are soluble in alcohol. *Isethionate of ammonia* forms transparent octohedra. The isethionates, when heated with hydrate of potash, evolve hydrogen, and a mixture of carbonate, oxalate, sulphate, and sulphite of the base is formed. Isethionic acid is also formed during the prolonged action of hydrated sulphuric acid upon alcohol or ether, and it is found in the residue obtained from the preparation of ether (989).

Parathionic Acid.—This acid is only known in combination with baryta. If the solution of sulphethylate of baryta be boiled for some time, it becomes acid, and deposits sulphate of baryta; on neutralizing the filtered liquid with carbonate of baryta a crystallizable parathionate of baryta is obtained which is not altered by boiling. When calcined it does not froth up like the isethionate, but yields vapours of heavy oil of wine, and burns steadily.

Another isomeric modification, termed by Regnault *althionic acid*, was procured by him from the residue of the preparation of ether. The baryta salt may be boiled when dilute without undergoing decomposition. By spontaneous evaporation this salt is obtained in radiated groups of delicate prisms.

(983) *Artificial formation of Alcohol from Olefiant Gas.*—The action of an excess of sulphuric acid upon alcohol at 325° has already been considered (399), as it is the usual process for obtaining olefiant gas. But the action of olefiant gas upon the acid is not less interesting. Faraday showed that when this gas is subjected to the action of concentrated sulphuric acid it is absorbed in considerable quantities. Berthelot has recently recalled attention to this observation, and he has succeeded in obtaining alcohol from olefiant gas by its means. One of his experiments consisted in filling a glass vessel, of about 2½ gallons in capacity, with pure olefiant gas, then introducing about 2lb. of pure oil of vitriol, and a few pounds of mercury to aid in bringing the acid into contact with the gas, when the mixture was agitated vigorously. After keeping the mixture in brisk agitation for some time, the gas was absorbed, and the colour of the acid became deepened. On diluting it with 6 times its bulk of water, submitting it to distillation and then rectifying from carbonate of potash, nearly two ounces of pure alcohol were obtained. Coal gas contains a considerable proportion of olefiant gas, and by agitating it with sul-

phuric acid it thus is rendered possible to procure alcohol from the gas in ordinary use for illuminating purposes.

(984) Olefiant gas combines readily with anhydrous sulphuric acid, producing a compound which may be regarded as *ethionic anhydride*. This compound is converted by water into hydrated ethionic acid; and the solution, when boiled, becomes decomposed, hydrated isethionic and sulphuric acids being produced. These decompositions may be readily traced, since the composition of these different compounds is the following:—

Ethionic anhydride	$C_4H_4,\ 2\ S_2O_6$
Hydrated ethionic acid . .	$2\ HO,\ C_4H_4,\ 2\ S_2O_6$
Isethionic acid	$HO,\ C_4H_5,\ S_2O_7$

Consequently the change which occurs, when hydrated ethionic acid is diluted with water and boiled is the following:—

$$\overbrace{2\ HO,\ C_4H_4,\ 2\ S_2O_6}^{\text{Hydrated Ethionic Acid.}} + 2\ HO = \overbrace{HO,\ C_4H_5,\ S_2O_7}^{\text{Isethionic Acid.}} + 2\ (\overbrace{HO,\ SO_3}^{\text{Sulphuric Acid.}}).$$

Ethionic Anhydride ($C_4H_4,\ 2\ S_2O_6$) was termed by Magnus, its discoverer, ***Sulphate of Carbyle***. It is prepared in the form of a white crystalline solid, by allowing the vapours of anhydrous sulphuric acid to come into contact with dry olefiant gas in a bent tube kept cool. The same compound is obtained when a tube charged with anhydrous alcohol is placed in a bottle fitted with an accurately ground stopper, containing anhydrous sulphuric acid; in the course of a few days white silky crystals of ethionic anhydride are formed in the tube. These crystals melt at 176°, and rapidly deliquesce by exposure to the air. They are soluble in water and in alcohol with great elevation of temperature, and cannot be recovered by evaporating the liquid, for they assimilate 2 equivalents of water, and become converted into the hydrated acid. The acid thus obtained, however, is not pure, since owing to the elevation of temperature a portion of ethionic is converted into isethionic acid. If the solution be neutralized by means of carbonate of baryta, and evaporated at a temperature below 212° until precipitation commences, ethionate of baryta is formed and may be obtained by adding absolute alcohol until the density of the solution is reduced to 0·900; the salt thus precipitated is impure ethionate of baryta: it must be redissolved in water, and again precipitated by the addition of alcohol. The ethionates are soluble in water, but insoluble in alcohol; they are decomposed by a temperature of 212°. If ethionate of baryta be heated strongly in a tube, it yields sulphuric acid and a sublimate of sulphur, the residue containing sulphate of baryta and sulphide of barium. The ethionates of potash, ammonia and soda may be readily obtained in crystals; they are prepared by decomposing a solution of ethionate of baryta by means of a solution of the sulphates of the different bases.

(985) *Other Vinic Acids*—Sulpho-acids may be obtained from the methylic, tritylic, tetrylic, amylic, and other alcohols, by treating them in a manner similar to that directed for procuring sulphethylic acid. Sulphomethylic acid may be obtained in crystals by evaporating its solution *in vacuo*. But the sulphuric is not the only acid which gives rise to these compound acids with the alcohols. The polybasic acids in general exhibit this power, even though their acid character may be but feeble. Carbonic, oxalic, and tartaric acids, for instance, may be made to yield compound acids analogous to the sulphethylic; and the same thing has been observed with sulphocarbonic acid (bisulphide of carbon). The tribasic acids, such as the phosphoric and arsenic, even form two acid compounds. The formulæ of some of these coupled acids in the ethylic series and of their salts are exhibited in the following table :—

Vinic Acids.	Hydrate.	Metallic Salt.
Carbethylic . . .	HO, C_4H_5O, C_2O_4	KO, C_4H_5O, C_2O_4
Xanthic or Sulpho-carbethylic	HO, C_4H_5O, C_2S_4	KO, C_4H_5O, C_2S_4
Oxalethylic . . .	HO, C_4H_5O, C_4O_6	KO, C_4H_5O, C_4O_6
Tartrethylic . .	$HO, C_4H_5O, C_8H_4O_{10}$	$KO, C_4H_5O, C_8H_4O_{10}$
Ethylsulphurous .	HO, C_4H_5O, S_2O_4	KO, C_4H_5O, S_2O_4
Phosphethylic . .	$2\,HO, C_4H_5O, PO_5$	$2\,BaO, C_4H_5O, PO_5 + 12$ aq
Diphosphethylic .	$HO, 2(C_4H_5O,)\,PO_5$	$PbO, 2(C_4H_5O)\,PO_5$
Diarsenethylic . .	$HO, 2(C_4H_5O,)\,AsO_5$?	$BaO, 2(C_4H_5O)\,AsO_5$

Similar compounds may be formed with the other alcohols.

Carbethylic acid cannot be isolated, but the carbethylate of potash is obtained by transmitting a current of carbonic acid through a solution of hydrate of potash in absolute alcohol. It is soluble in alcohol, and forms pearly scales which are decomposed by water into bicarbonate of potash and alcohol.

Xanthic or *Sulphocarbethylic Acid.*—Xanthate or sulphocarbethylate of potash is a salt which crystallizes in needles. It is easily obtained by adding to an alcoholic solution of potash, a quantity of bisulphide of carbon, until the alkaline reaction has disappeared: on exposing the solution to a cold of 32°, the salt is deposited in needles; and the carbosulphethylic acid may be obtained from this salt by decomposing a concentrated solution of it with hydrochloric acid, when it separates as a heavy oily liquid.

Oxalethylic Acid.—The oxalethylate (oxalovinate) of potash is obtained by decomposing oxalic ether dissolved in alcohol by a quantity of an alcoholic solution of potash sufficient to combine with one half of the oxalic acid which it contains. The alcoholic solution yields pearly scales of the salt, which, when decomposed with fluosilicic acid, furnishes free oxalethylic acid.

Ethylsulphurous or *sulphoethylolic acid* is obtained by acting upon mercaptan ($C_4H_6S_2$) (995) with nitric acid (of sp. gr. 1·23) so long as decomposition continues to take place: violent reaction occurs, attended with the escape of nitrous fumes. The excess of nitric acid is expelled by evaporating the liquid over the water bath, and the residue, after dilution, is saturated with carbonate of lead; the filtered liquid is evaporated, and the ethylsulphite of lead is allowed to crystallize. If this salt be decomposed by means of sulphuretted hydrogen, the acid is set at liberty, and, by concentration over the water bath, it may be obtained in transparent crystals, which have an acid disagreeable taste.

Phosphethylic or *Phosphovinic Acid.*—When equal parts of alcohol and syrupy phosphoric acid are heated together, combination takes place; phosphethylate of baryta may be obtained by saturating the liquid with carbonate of baryta, distilling off the excess of alcohol and then filtering the solution and allowing it to crystallize. On decomposing this salt cautiously by the addition of sulphuric acid, the phosphethylic acid is liberated.

Diphosphethylic Acid.—By adding anhydrous phosphoric acid gradually to absolute alcohol, a mixture of phosphethylic and diphosphethylic acid is formed. On the addition of carbonate of lead, the phosphethylic acid and the excess of phosphoric acid are removed, whilst the diphosphethylate of lead remains in solution, and may be obtained in crystals by evaporation; if the acid be required in a separate form, it may be procured by passing sulphuretted hydrogen through a solution of the lead salt. When the diphosphethylate of lead is subjected to a heat of about 370°, it is decomposed, and phosphoric ether ($3\,C_4H_5O, PO_5$) distils over:—

$$\overbrace{2(\mathrm{PbO}, (\mathrm{C_4H_5O})_2, \mathrm{PO_5})}^{\text{Diphosphethyl. Lead.}} = \overbrace{3(\mathrm{C_4H_5O}), \mathrm{PO_5}}^{\text{Phosphoric Ether.}} + \overbrace{2\,\mathrm{PbO}, \mathrm{C_4H_5O}, \mathrm{PO_5}}^{\text{Phosphethyl. Lead.}}.$$

§ IV. THE ETHERS—SIMPLE, DOUBLE, AND COMPOUND.

(986) *General Remarks on the Ethers.*—The ethers admit of being conveniently subdivided into three classes, viz., 1. The *simple ethers,* of which ordinary ether (C_4H_5O, C_4H_5O) is the best representative. 2. The *double ethers,* discovered by Williamson, such as the methyl-amylic (C_2H_3O, $C_{10}H_{11}O$), and the ethyl-octylic (C_4H_5O, $C_{16}H_{17}O$). 3. The *compound ethers,* which may either contain the elements of a simple ether, and of an anhydrous oxy-acid, such as nitric ether (C_4H_5O, NO_5), acetate of amyl ($C_{10}H_{11}O$, $C_4H_3O_3$), and formiate of methyl (C_2H_3O, C_2HO_3): or they may be produced by the action of a hydracid, such as the hydrochloric, upon one of the alcohols; hydrochloric ether (C_4H_5Cl) and hydriodic ether (C_4H_5I) affording examples of this kind.

(1) The *simple ethers,* which contain oxygen, are usually formed by the distillation of the alcohol with sulphuric acid; in this case the distilled liquid may be viewed as a compound derived from the alcohol by the removal of an equivalent of water. There are, however, reasons for thinking that the true relation between the alcohol and the ether is of a different nature; but, supposing this hypothesis to be correct, the simple ethers which contain oxygen might be considered to consist of oxides of particular hydrocarbons (which form the radicles of the ethers), whilst the alcohols would be hydrated oxides of the same bodies. Thus Liebig represents ordinary (ethylic) ether as $(C_4H_5)O$, and ordinary alcohol as $(C_4H_5)O, HO$. Berzelius suggested, on the other hand, that ether and alcohol might each be formed in a similar manner, and recent researches, particularly those of Williamson, have rendered it highly probable that the molecular constitution of both alcohol and ether is similar, so that both may be regarded as compounds formed upon the type of water $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$, in which case alcohol would be water in which one-half of its hydrogen has been displaced by ethyl; and ether would be water in which both halves of the hydrogen have been displaced by ethyl; thus,*

$$\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2}^{\text{Ether.}}$$

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* It will be recollected that Gerhardt doubles the equivalents of oxygen, carbon, and sulphur; a view adopted by Williamson, Brodie, and others, and that in consequence these chemists regard water as $\left.\begin{matrix}H\\H\end{matrix}\right\}O$. Gerhardt's double

This doubling of the formulæ of ether has become necessary in consequence of Williamson's discovery of the existence of double ethers, the general properties of which we proceed to examine.

(2) *Double Ethers.*—When sodium or potassium is added gradually to anhydrous alcohol, a brisk action occurs, the temperature rises rapidly, and the metal is dissolved, whilst an extrication of pure hydrogen gas takes place, and a fusible, crystallizable, deliquescent compound is formed, which has received the name of *sodium-alcohol* (or potassium-alcohol), or of *ethylate of soda* (or of potash); its composition being such that it may be regarded as alcohol in which one equivalent of hydrogen has been displaced by one of sodium or of potassium; thus, if sodium be used:—

$$\overbrace{C_4H_5O,\ HO}^{\text{Alcohol.}} + Na = \overbrace{C_4H_5O,\ NaO}^{\text{Sodium Alcohol.}} + H$$

This and the subsequent reactions may, perhaps, be more readily traced by throwing the equations into a form similar to the following:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\ H\end{matrix}\right\}}^{\text{Alcohol.}}O_2 + Na = \overbrace{\left.\begin{matrix}C_4H_5\\ Na\end{matrix}\right\}}^{\text{Sodium Alcohol.}}O_2 + H$$

The action of sodium or potassium upon the other alcohols is of

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equivalents are here given in italics to distinguish them from those in ordinary use. The chemists who adopt Gerhardt's views further regard the smallest particles of hydrogen as it exists in the gaseous state, not as consisting of the elementary molecules of hydrogen H, but rather as being each composed of two molecules, $\left.\begin{matrix}H\\ H\end{matrix}\right\}$ thus making hydrogen gas a ***hydride of hydrogen;*** the oxygen in the molecule of water $\left(\left.\begin{matrix}H\\ H\end{matrix}\right\} O\right)$ being indivisible, but the hydrogen being divisible into two portions; each portion being supposed to be capable of displacement by an equivalent of various metals, such as potassium, sodium, calcium, &c.; hydrate of potash being $\left.\begin{matrix}H\\ K\end{matrix}\right\} O$, slaked lime $\left.\begin{matrix}H\\ Ca\end{matrix}\right\} O$, and so on. In like manner the molecules of hydrogen are supposed to be separately displaceable by a molecule of ethyl, (C_2H_5); of methyl, (CH_3); of amyl, (C_5H_{11}), &c.; so that the formulæ of water, alcohol, and ether will be respectively—

$$\overbrace{\left.\begin{matrix}H\\ H\end{matrix}\right\}}^{\text{Water.}} O \quad ; \quad \overbrace{\left.\begin{matrix}C_2H_5\\ H\end{matrix}\right\}}^{\text{Alcohol.}} O \quad ; \quad \overbrace{\left.\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\right\}}^{\text{Ether.}} O$$

This atomic hypothesis of Gerhardt's is not essential to the view of the formation of ether given above, but it tends considerably to simplify it. Sulphuric acid, it must be borne in mind, is regarded by Gerhardt as dibasic, and hence he would represent it as $\left.\begin{matrix}H\\ H\end{matrix}\right\} O,\ SO_2$; and sulphethylic acid as $\left.\begin{matrix}C_2H_5\\ H\end{matrix}\right\} O,\ SO_2$. See also (1102).

an analogous nature; for example, a similar result is obtained when wood spirit is treated with sodium:—

$$\overbrace{\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O_2}^{\text{Methyl Alcohol.}} + Na, \text{ becoming } \overbrace{\left.\begin{matrix}C_2H_3\\Na\end{matrix}\right\}O_2}^{\text{Sodium Methylcohol.}} + H.$$

Now, if the sodium compound of alcohol be sealed up in a tube with an equivalent amount of iodide of methyl, and heat be applied, mutual decomposition occurs; iodide of sodium being formed, whilst the molecule of methyl takes the place of the sodium in the alcohol, and thus a double ether, the ethylmethylic, is formed:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\Na\end{matrix}\right\}O_2}^{\text{Sodium Alcohol.}} + \overbrace{\left.\begin{matrix}C_2H_3\\I\end{matrix}\right\}}^{\text{Iodide of Methyl.}} = \overbrace{\left.\begin{matrix}C_4H_5\\C_2H_3\end{matrix}\right\}O_2}^{\text{Ethylmethylic Ether.}} + \overbrace{\left.\begin{matrix}Na\\I\end{matrix}\right\}}^{\text{Iodide of Sodium.}}$$

A reaction of a similar kind is obtained if iodide of amyl be made to act upon the sodium-alcohol; amyl-ethylic ether being formed in this case, as follows:—

$$\overbrace{C_4H_5O,\ NaO}^{\text{Sodium Alcohol.}} + \overbrace{C_{10}H_{11}I}^{\text{Iodide of Amyl.}} = \overbrace{(C_4H_5O,\ C_{10}H_{11}O)}^{\text{Amyl-ethylic Ether.}} + NaI; \text{ or}$$

$$\left.\begin{matrix}C_4H_5\\Na\end{matrix}\right\}O_2 + \left.\begin{matrix}C_{10}H_{11}\\I\end{matrix}\right] = \left.\begin{matrix}C_{10}H_{11}\\C_4\,H_5\end{matrix}\right\}O_2 + NaI.$$

Several other double ethers have been formed by analogous methods. An equivalent of each of these ethers yields 4 volumes of vapour, as may be seen by comparing the theoretical with the experimental numbers:—

		Boiling point. ° F.	Specific Gravity.	
			Theory.	Experiment
Methyl-ethylic Ether	$C_2H_3O,\ C_4\,H_5\,O$	51·8	2·084	2·158
Methyl-amylic Ether	$C_2H_3O,\ C_{10}H_{11}O$	197·6	3·546	3·74
Amyl-ethylic Ether .	$C_4H_5O,\ C_{10}H_{11}O$	233·6	4·031	4·042

Now, if iodide of ethyl be substituted for the iodide of amyl, or iodide of methyl, in the foregoing experiment the iodide of ethyl also is decomposed by the sodium-alcohol, and ordinary ether is produced:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\Na\end{matrix}\right\}O_2}^{\text{Sodium Alcohol.}} + \left.\begin{matrix}C_4H_5\\I\end{matrix}\right\} = \overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2}^{\text{Ethylic Ether.}} + NaI.$$

The conclusion, therefore, appears to be inevitable, that the molecule of common ether must likewise be analogous in its construction to nolecules of the double ethers. Moreover, if the equivalent of r be regarded as composed only of C_4H_5O, it yields only two nes of vapour; whereas, if the equivalent be taken as ${}_5O$, C_4H_5O), it yields four volumes of vapour, like alcohol the other organic compounds.

(3) *Compound Ethers.*—When one of the alcohols is brought contact with a hydrated monobasic acid, the two bodies react n each other, two equivalents of water are eliminated, and the ments of the anhydrous acid and of the ether unite together, and m a compound ether. Thus, when acetic acid is subjected to tillation with ordinary alcohol, acetic ether is produced:—

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2}^{\text{Acetic Acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} = \overbrace{\left.\begin{matrix}C_4H_3O_2\\C_4H_5\end{matrix}\right\}O_2}^{\text{Acetic Ether.}} + \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}}.$$

double decomposition occurs in this case, as in the foregoing, e basic hydrogen of the acetic acid changing places with the olecule of ethyl contained in the alcohol. When the affinities f the acid are not very strong, the reaction is facilitated by ixing one of salts of the acid with alcohol, and then liberating he acid by the agency of sulphuric acid; in this manner formic ether is readily obtained by distilling a mixture of dry formiate of soda, alcohol, and concentrated sulphuric acid, although hydrated formic acid and alcohol, when distilled together have but a comparatively small action upon each other. Berthelot obtains the reaction of the organic acid upon the alcohol in most cases, without the intervention of a stronger acid, by exposing the alcohol and the acid in sealed tubes for some hours to a temperature varying from 212° to 480°.

Many compound ethers, such as the butyric, the benzoic, and the palmitic, may, according to M. Berthelot, be obtained by sealing up a mixture of the hydrated acid with the simple oxygen ether in a tube, and exposing it to a temperature of about 750°. In this case only one equivalent of water is separated from the hydrated acid. (*Ann. de Chimie*, III. xli. 432.)

Other modes may be adopted for obtaining the compound ethers. When the oxychlorides of the monobasic acids (1097) are heated with alcohol, a compound ether of the corresponding monobasic acid is obtained: thus benzoic oxychloride (chloride of benzoyl) yields benzoic ether when heated with anhydrous alcohol:—

$$\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\Cl\end{matrix}\right\}}^{\text{Benzoic Oxychlor.}} + \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} = \overbrace{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}^{\text{Hydrochloric Acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\C_{14}H_5O_2\end{matrix}\right\}O_2}^{\text{Benzoic Ether.}}.$$

The distillation of the concentrated aqueous solution of a vinic salt, such as the sulphomethylate or sulphethylate of potash or of lime, with a concentrated solution of the sulphide, selenide, telluride, or cyanide of potassium, furnishes an easy method of obtaining the corresponding ether with sulphur, selenium, tellurium, or cyanogen. Thus if the cyanide of methyl were required, the reaction would be the following:—

$$\overbrace{KO,\ C_2H_3O,\ S_2O_6}^{\text{Sulphomethylate of Potash.}} + KCy = \overbrace{C_2H_3Cy}^{\text{Cyanide of Methyl.}} + \overbrace{2\ (KO,\ SO_3)}^{\text{Sulphate of Potash.}}.$$

Other modes of preparing particular ethers are adopted; these will be noticed when the ethers to which they apply are described.

The ethers of the hydracids are readily formed by the direct action of these acids upon the alcohols; hydrochloric ether, for instance, may be formed by saturating alcohol with hydrochloric acid gas, and submitting the mixture to distillation:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} + \overbrace{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}^{\text{Hydrochloric acid.}} = \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}} + \overbrace{\left.\begin{matrix}C_4H_5\\Cl\end{matrix}\right\}}^{\text{Hydrochloric Ether.}}$$

The molecule of ethyl in the alcohol, and that of hydrogen in the acid, change places, and hydrochloric ether and water are produced by double decomposition.

Advantage is taken of the facility with which the hydracids act upon the alcohols, in order to prepare compound ethers with acids of comparatively feeble affinities. Thus if it be desired to obtain ethers of the fatty acids, such as palmitic ether for example, the palmitic acid is dissolved in alcohol, and a current of hydrochloric acid is transmitted, whilst the alcohol is gently heated. After the reaction has terminated, the product is washed with hot water; and the palmitic ether being insoluble in water, is readily separated from the mixture. It appears that hydrochloric ether is first formed, and this afterwards undergoes double decomposition when heated with the fatty acid:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} + \left.\begin{matrix}H\\Cl\end{matrix}\right\} = \left.\begin{matrix}H\\H\end{matrix}\right\}O_2 + \overbrace{\left.\begin{matrix}C_4H_5\\Cl\end{matrix}\right\}}^{\text{Hydrochloric Ether.}};\ \text{and}$$

$$\overbrace{\left.\begin{matrix}C_4H_5\\Cl\end{matrix}\right\}}^{\text{Hydrochloric Ether.}} + \overbrace{\left.\begin{matrix}C_{32}H_{31}O_2\\H\end{matrix}\right\}O_2}^{\text{Palmitic Acid.}} = \left.\begin{matrix}H\\Cl\end{matrix}\right\} + \overbrace{\left.\begin{matrix}C_{32}H_{31}O_2\\C_4\ H_5\end{matrix}\right\}O_2}^{\text{Palmitic Ether.}}.$$

The ethers of the dibasic acids, when converted into vapour, yield only two volumes of vapour for each equivalent of oxide of ethyl which they contain: so that if four volumes of vapour be taken as the representative of an equivalent of those compounds, the formula of the oxalic, carbonic, and succinic ethers, must be taken as containing one equivalent of the dibasic acid and two equivalents of oxide of ethyl; the formula of carbonic ether being written ($2\ C_4H_5O,\ C_2O_4$).

(987) *Nature of the Compound Ethers.*—Liebig has proposed to consider the compound ethers as salts, in which the acid is supposed to be combined with an organic oxide instead of a metallic one; acetic ether, for example, being regarded as acetate of oxide of ethyl; $(C_4H_5)\ O,\ C_4H_3O_3$. The organic oxide, however, cannot readily be displaced by a metallic oxide,—as oxide of ammonium can from its salts, by means of oxide of potassium; and the properties of the ethers, as well as the mode of their formation, are in reality more allied to those of the amides than to the ordinary salts. Indeed, they present a striking analogy with the amides (1045), as may be seen on comparing them in a few leading particulars.

The amides are formed by the union of ammonia with the acids, whilst an elimination of water takes place. Benzamide, for instance, consists of the elements of benzoate of ammonia, minus water; thus—

$$\overset{\text{Ammonia.}}{\left.\begin{array}{c}H\\H\\H\end{array}\right\}N} + \overset{\text{Benzoic Acid.}}{\left.\begin{array}{c}C_{14}H_5O_2\\H\end{array}\right\}O_2} = \overbrace{\left.\begin{array}{c}C_{14}H_5O_2\\H\\H\end{array}\right\}}^{\text{Benzamide.}}N + \overbrace{\left.\begin{array}{c}H\\H\end{array}\right\}}^{\text{Water.}}O_2$$

Benzoic ether contains the elements of benzoic acid and alcohol, minus the same number of equivalents of water:—

$$\overbrace{\left.\begin{array}{c}C_4H_5\\H\end{array}\right\}}^{\text{Alcohol.}}O_2 + \overbrace{\left.\begin{array}{c}C_{14}H_5O_2\\H\end{array}\right\}}^{\text{Benzoic Acid.}}O_2 = \left.\begin{array}{c}H\\H\end{array}\right\}O_2 + \overbrace{\left.\begin{array}{c}C_{14}H_5O_2\\C_4\,H_5\end{array}\right\}}^{\text{Benzoic Ether.}}O_2$$

The amides, when treated with hydrating agents, as for instance when boiled with alkalies, slowly become hydrated; ammonia, and the acid from which they were formed, being reproduced: and in like manner the compound ethers, when treated with a solution of potash, are resolved into alcohol, and the acid whence they were formed. Indeed, this change of the compound ethers into alcohol and the hydrated acid often takes place by mere prolonged contact with water, and this decomposition is greatly accelerated by the presence of a small quantity of free acid, particularly if the temperature be raised to the boiling point.

Again, the dibasic acids form with amidogen *amidic* acids, which may be regarded as acids in which one half of the acid has experienced a reduction to the form of amide by the action of 1 equivalent of ammonia; and the vinic acids, in like manner, may be viewed as dibasic acids in which one half the acid has been converted into a compound ether by the action of 1 equivalent of one of the alcohols. Oxamic and oxalethylic (oxalovinic) acids, for instance, may be represented respectively as compounds of oxalic acid with oxamide and with oxalic ether:—

$$\overbrace{2\,(H_2NC_2O_2)}^{\text{Oxamide.}} + \overbrace{2\,HO,\ C_4O_6}^{\text{Oxalic Acid.}} = \overbrace{2\,(HO,\ (H_2NC_2O_2)\ C_2O_3)}^{\text{Oxamic Acid.}}.$$

$$\overbrace{2\,C_4H_5O,\ C_4O_6}^{\text{Oxalic Ether.}} + \overbrace{2\,HO,\ C_4O_6}^{\text{Oxalic Acid.}} = \overbrace{2\,(HO,\ C_4H_5O,\ C_4O_6.)}^{\text{Oxalethylic Acid.}}$$

(988) *Chemical Properties of the Ethers.*—The simple ethers, and the compound ethers of the monobasic acids, may generally be volatilized without undergoing decomposition; but their boiling point rises as the number of equivalents of the hydrocarbon (C_2H_2) which they contain increases. A similar observation applies to the boiling point of compound ethers of different alcohols derived from the same acid, as well as to ethers derived from the same alcohol but containing different but homologous acids. The ethers are generally sparingly soluble in water, but they are readily dissolved by alcohol and by ordinary ether. None of the simple ethers have as yet been detected ready formed in the vegetable kingdom, but the compound ethers appear to be not unfrequently present in fruits and some other parts of plants, which occasionally owe their fragrance to these bodies. The *oil of winter green* is a salicylate of methyl $C_2H_3O,\ C_{14}H_5O_5$, and, as Cahours has shown, it may be artificially produced by the combination of oxide of methyl with salicylic acid. Many of the artificial essences sold by the perfumers and confectioners consist of these ethers dissolved in alcohol; for it is a remarkable circumstance, that the pure ethers often have a repulsive odour, which is very different to that which they possess when largely diluted with alcohol. The so-called *pear oil*, or *essence of Jargonelle pear*, is an alcoholic solution of acetate of amyl $C_{10}H_{11}O,\ C_4H_3O_3$. *Apple oil* is a similar preparation of valerianate of amyl $C_{10}H_{11}O,\ C_{10}H_9O_3$. *Pine-apple oil* is simply butyric ether $C_4H_5O,\ C_8H_7O_3$ diluted with alcohol (Hofmann, *Ann. de Chimie*, III. xxxiv. 325). *Essence of melons* is the ethyl compound of one of the acids of cocoa-nut oil. *Essence of quinces* is dilute pelargonic ether $C_4H_5O,\ C_{18}H_{17}O_3$; and the

peculiar odour of wine is found to be due to an ether, termed by Liebig and Pelouze, who discovered it, *œnanthic ether*, (from οἶνος, wine,) C_4H_5O, $C_{14}H_{13}O_2$ (?), but which, according to Delffs, is simply pelargonic ether. This ether is stated to be the basis of *Hungarian wine oil*, which has been sold for flavouring brandy, at the rate of sixty-nine dollars per pound.—(Johnston.)

(*a*) *Ordinary Ether—Theory of Etherification.*

(989) ETHER; *Ethylic* or *Vinic Ether*, also improperly called *Sulphuric Ether* (C_4H_5O, C_4H_5O). *Sp. gr. of liquid* at 32° 0·7365; *of vapour* 2·586.

Preparation.—Formerly ether was prepared by mixing 2 measures of alcohol and 1 measure of sulphuric acid, and distilling until it began to blacken; then a quantity of alcohol, equal to half that originally used, was added to the residue in the retort, and the distillation was again proceeded with until the ether ceased to come over. The method at present in general use for the preparation of ether is that known as the "continuous process" of Boullay. It consists in mixing together equal measures of alcohol (sp. gr. 0·830), and of concentrated sulphuric acid; the mixture is submitted to distillation in a capacious retort, which must be connected with an efficient condenser. Through the tubulure of the retort a tube is introduced, which is in communication with a reservoir of alcohol, designed to maintain a supply of spirit sufficient to keep the amount of liquid at a uniform level in the retort during the course of the subsequent distillation. The temperature is then rapidly raised so as to maintain the mixture in steady ebullition. The liquid which passes over consists almost entirely of ether and water, mixed with a small portion of alcohol, which has distilled over unchanged.

This process may go on without interruption until a quantity of alcohol, about thirty times as great as that originally taken, has become converted into ether. Isethionic acid is gradually formed in the residue.

Mitscherlich distilled a mixture of 1 part of absolute alcohol with 2 parts of sulphuric acid, consisting of 5 parts of oil of vitriol diluted with 1 part of water (HO, SO_3, HO, sp. gr. 1·780 nearly), the original volume of liquid in the retort being maintained by a gradual supply of absolute alcohol; he found that for every 100 parts of alcohol consumed, about 65 of ether, 17 of water, and 18 of undecomposed alcohol were obtained: the quantity of alcohol which distils depending upon the rapidity with which the operation is conducted; the more quickly it is performed the larger being the quantity of alcohol. When absolute alcohol is used, for every 65 parts of ether obtained, 15·4 of water should be produced, the slight excess observed depending upon the presence of traces of water in the alcohol. With a more dilute alcohol the proportion of water which passes over is greater, the excess corresponding with the amount present in the alcohol. The temperature most favourable to the formation of ether is from 284° to 290°. At a temperature of 320° the disengagement of sulphurous acid mixed with olefiant gas and oil of wine commences. If a sulphuric acid much more dilute than one of sp. gr. 1·632 ($HO, SO_3, 2\,HO$) be employed, the excess of water gradually distils over with the alcohol, which undergoes little change until the liquid has become sufficiently concentrated to allow the boiling point to rise to 284°, after which ether is formed as usual. Alcohol may also be converted into ether by heating it with phosphoric, arsenic, and perchloric acids, as well as by means of bichloride of tin, chloride of zinc, fluoride of boron, and by several other processes which will be further considered when the theory of etherification is passed under review (990).

In order to purify the crude ether, it should be agitated with an equal bulk of water, containing $\frac{1}{16}$th of its weight of carbonate of potash in solution; the water combines with the alcohol, and the potash unites with any sulphurous acid that may have distilled over: the liquid separates into two layers, the upper of which consists of ether holding a little water in solution. The ether may be freed from water by allowing it to stand for a day or two upon quicklime, or upon chloride of calcium: it is then to be rectified by the heat of a water-bath, and condensed in vessels kept cool with ice-cold water.

Properties.—Pure ether is an extremely limpid, colourless, transparent, volatile liquid, of high refracting power; it possesses a powerful, penetrating, and peculiar odour, and a taste at first fiery, but afterwards cooling: if taken internally it produces stimulating and intoxicating effects. Its vapour, when inhaled, at first occasions exhilaration, speedily followed by complete insensibility to pain; owing to this property it was at one time extensively administered during surgical operations, to diminish the sufferings of the patient; but its employment for this purpose has been superseded by the use of chloroform, the effects of which are more speedy and certain, and are attended with less excitement to the system. Ether has a sp. gr. of 0·724 at 55°. It boils at 94°8 F., and freezes at about —24°. From its great volatility, and the consequent depression of temperature furnished by its rapid evaporation, it is frequently employed for producing cold artificially. Ether is dissolved freely by alcohol, but sparingly by water. When agitated with an equal bulk of water, it dissolves about $\frac{1}{5}$th of its volume of water, while the water takes $\frac{1}{8}$th of its bulk of ether. Ether is employed to some extent as a solvent for fatty bodies, and is used in the proximate analysis of organic matters for separating the fats or oils which they contain from other substances which are not soluble in this menstruum. Iodine, sulphur, and phosphorus, are dissolved by ether. Ammoniacal gas, and deutoxide of nitrogen, are also freely absorbed by it: certain metallic salts are likewise dissolved by it; among these are bichloride of platinum, and sesquichloride of iron; with bichloride of tin it forms a volatile crystalline compound $(C_4H_5O, C_4H_5O,)\ SnCl_2$. Chloride of mercury and terchloride of gold are also freely soluble in ether; these two compounds may be separated from their solutions in water by agitation with ether, and they rise with it to the surface when left at rest.

Ether is extremely inflammable, and as it is also very volatile and furnishes a vapour of considerable density, great care must be taken not to pour it out in the vicinity of a flame; many serious accidents having arisen from a neglect of this precaution. In certain proportions its vapour forms an explosive mixture with air or oxygen. When burned with a sufficient supply of oxygen it produces only water and carbonic acid. Its flame is more luminous than that of alcohol, and it deposits charcoal on cold bodies which are introduced into it. When passed through ignited tubes it is decomposed; charcoal is deposited, and aldehyd is found among the products. If burned at a lower heat with insufficient access of air, it yields a mixture of aldehyd with acetic acid and acetal; but aldehyd is the predominating ingredient: this formation of aldehyd is easily explained, since the substitution of two equivalents of oxygen for two of hydrogen in the formula for ether, furnishes the elements of two equivalents of aldehyd, the hydrogen combining with two more equivalents of oxygen, and being eliminated in the form of water:—

$$\overbrace{(C_4H_5O,\ C_4H_5O)}^{\text{Ether.}} + 4\,O = 2\ \overbrace{(C_4H_4O_2)}^{\text{Aldehyd.}} + 2\ HO.$$

If ether be kept in vessels partially filled with air, it gradually absorbs oxygen, and acetic acid is formed. When treated with concentrated sulphuric acid, ordinary ether becomes converted into sulphethylic acid; and if this liquid be boiled, sweet oil of wine mingled with sulphurous acid passes over, the mixture blackens considerably, and ethionic and isethionic acids are formed in the retort.

Nitric acid acts powerfully upon ether with the aid of heat, forming carbonic, acetic, and oxalic acids.

If ether be saturated with hydrochloric acid and distilled, hydrochloric ether is the product. Chlorine converts it into various substitution compounds, and produces aldehyd, chloral, and hydrochloric ether, whilst hydrochloric acid is evolved in abundance.

Potassium and sodium decompose ether slowly, and liberate hydrogen gas.

(990) *Theory of Etherification.*—In the process of preparing ether from alcohol by the agency of sulphuric acid, it will be observed that a small quantity of this acid converts an indefinite quantity of alcohol into ether and water. The explanations which have been offered to account for the formation of ether by the action of sulphuric acid are very numerous. Most chemists, however, now admit with Liebig, that the essential change may be divided into two stages, the first of which consists in the formation of sulphethylic acid, and the second in the decomposition of this acid into sulphuric acid, water, and ether. When fresh alcohol is added to the mixture, a new quantity of sulphethylic acid is formed with the sulphuric acid liberated during the previous distillation; this sulphethylic acid in its turn undergoes decomposition into ether, water, and sulphuric acid, and thus the same portion of sulphuric acid continues the etherification for an indefinite period. The following ingenious experiment by Williamson goes far towards proving the occurrence of this successive formation and decomposition of sulphethylic acid during the process of etherification. A mixture of sulphuric acid and amylic alcohol was prepared, so as to obtain sulphamylic acid (HO, $C_{10}H_{11}O$, 2 SO_3) (one of the homologues of sulphethylic acid); this mixture was placed in a retort and then submitted to distillation, supplying it with ordinary alcohol, as in the continuous process of making ether already described. The distillation was continued until the liquid which passed over contained only ordinary ether, without any compound of fousel oil. On examining the residue in the retort it was found to contain sulphethylic acid only, the sulphamylic acid having entirely disappeared, a double ether (amy[illegible]er, C_4H_5O, $C_{10}H_{11}O$) being

found in the first portions of the distilled liquid. The successive stages of this action may be traced as follows :—

$$\text{(1)}\ \overbrace{\left.\begin{matrix}C_{10}H_{11}\\H\end{matrix}\right\}O_2,\ S_2O_6}^{\text{Sulphamylic Acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{1st eq. Alcohol.}} = \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2,\ S_2O_6}^{\text{Sulphuric Acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\C_{10}H_{11}\end{matrix}\right\}O_2}^{\text{Amylethylic Ether.}}.$$

$$\text{(2)}\ \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2,\ S_2O_6}^{\text{Sulphuric Acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{2nd eq. Alcohol.}} = \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2,\ S_2O_6}^{\text{Sulphovinic Acid.}} + \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}}.$$

$$\text{(3)}\ \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2,\ S_2O_6}^{\text{Sulphovinic Acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{3rd eq. Alcohol.}} = \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2,\ S_2O_6}^{\text{Sulphuric Acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2}^{\text{Ether.}}.$$

Now, since two successive stages have been proved to occur during the formation of this double ether, and since they have been also traced with other double ethers, it appears highly probable that similar steps may attend the formation of common ether by the continuous process, in which it may be supposed that the first reaction takes place between one double equivalent of sulphuric acid* and an equivalent of alcohol; one of the molecules of basic hydrogen in the acid exchanging places with the ethyl of the ether, thus forming one equivalent of sulphethylic acid and one of water, as follows :—

$$\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2,\ S_2O_6}^{\text{Sulphuric Acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} = \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2,\ S_2O_6}^{\text{Sulphethylic Acid.}} + \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}},$$

in the second stage of the reaction, the newly-formed sulphethylic acid, and a new equivalent of alcohol undergo double decomposition, the basic hydrogen of the alcohol being substituted for the equivalent of ethyl contained in the sulphethylic acid; an equivalent ether being produced, whilst the double equivalent of sulphuric acid is again set at liberty to perform a similar round with fresh portions of alcohol :—

$$\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2,\ S_2O_6}^{\text{Sulphethylic Acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{2nd eq. Alcohol.}} = \overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2}^{\text{Ether.}} + \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2,\ S_2O_6}^{\text{Sulphuric Acid.}}$$

The principal difficulty in admitting this view arises from the paradoxical circumstance, 'that the sulphethylic acid should be produced and decomposed under precisely similar circumstances of temperature. Mitscherlich, Berzelius, and Graham, therefore simply consider that sulphuric acid has the power of producing a decomposition of alcohol into ether and water, by some unexplained action, to which the terms contact-action and catalytic force have been applied. (859 *et seq.*) Mitscherlich even considers the formation of sulphethylic acid as an accidental circumstance not connected with the formation of ether. The following is one of his experiments:—A mixture of sulphuric acid and water was prepared of such a strength that it boiled at 290° (sp. gr. 1·52), and the vapour of alcohol heated to 212° was transmitted into it whilst the acid was kept at the boiling point. After the alcohol vapours had been transmitted for a short interval, ether and water began to collect in the receiver, and continued to do so as long as the current of vapour was kept up, four-fifths of the alcohol undergoing decomposition, about one-fifth only passing over unchanged, and this portion probably escaped simply because, from the rapidity of the current of vapour, it did not come completely into contact with the acid. Now, it is obvious, from the evolution of latent heat which accompanies the condensation of vapour, that the points in which the alcohol vapour were condensed by the acid must have been considerably above 290°; but as sulphethylic acid is decomposed below this temperature, Mitscherlich argues that it is impossible, that under these circumstances any of this acid could have been formed, and subsequently decomposed. If the dilution of the acid were less considerable (sp. gr. 1·61), and only sufficient to reduce the boiling point to 325° or 330°, the alcohol vapour when transmitted through the boiling liquid was converted into olefiant gas and water (399); (C_4H_5O, HO) becoming $C_4H_4 + 2\,HO$; scarcely any ether being evolved during the reaction, and no deposit of carbon occurring.

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* If sulphuric acid be dibasic as Gerhardt assumes, and as the progress of research appears to prove, its formula will require to be doubled, so that it may be written $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2,\ S_2O_6$; or 2 $HO,\ S_2O_6$.

Graham has also made some experiments which throw considerable doubt upon the necessity of the successive formation and decomposition of sulphethylic acid in the preparation of ether (*Quart. Journ. Chem. Soc.* iii. 24). In these experiments, mixtures of alcohol and sulphuric acid, in different proportions, were enclosed in sealed tubes, and subjected for an hour to a temperature ranging from 284° to 352°. It was found that when 1 volume of oil of vitriol was added slowly to 4 volumes of alcohol (sp. gr. 0.841), then sealed up and heated, the liquid separated into two layers; the upper one occupied one-third of the bulk of the whole liquid, and was nearly pure ether; the lower contained a mixture of water, alcohol, and sulphuric acid, but scarcely any sulphethylic acid; the lower stratum of the liquid had a slight yellow tinge, but the upper layer was colourless. When 8 measures of alcohol were mixed with 1 of acid, the proportion of ether which floated was still equal to one-third of the bulk of the entire liquid. On the other hand, when the formation of sulphethylic acid was favoured by reducing the proportion of alcohol, the production of ether became insignificant. Thus, when the quantity of alcohol only amounted to twice the bulk of the acid, the liquid assumed an earthy brown colour after heating, and only a film of ether separated on standing; and when equal volumes of acid and alcohol were used, a black, opaque, gummy liquid was formed without any perceptible stratum of ether.

When glacial phosphoric acid, and when biphosphate of soda were substituted for sulphuric acid, no ether was formed even though the mixture was heated to 360°. Chloride of zinc, under similar circumstances, produced only traces of ether. But when crystallized bisulphate of soda containing a slight excess of acid was employed, it was found to etherize twice its bulk of alcohol as effectually as free sulphuric acid.

A still more striking experiment was made by taking a portion of the ordinary ether mixture, viz., 100 parts of oil of vitriol, 48 of alcohol (sp. gr. 0·841), and 18·5 of water, placing it in a sealed tube, and heating for an hour to 290°. Sulphethylic acid was produced, but no ether was formed. It was then divided into two portions, to one of which half its bulk of alcohol was added, to the other, half its bulk of water; the two were sealed up in separate tubes and again heated. No ether was formed in the tube to which water was added, while in the other, the formation of ether was considerable. The sulphethylic acid was incapable of yielding ether even when treated with water; but it could etherize alcohol added to it, just as bisulphate of soda had done.

Various salts are capable of etherifying alcohol, if heated strongly with it under pressure. M. Reynoso states, that the several crystallized neutral sulphates, isomorphous with sulphate of magnesia, when sealed up with alcohol in tubes and heated to 464°, effect a partial etherification of the alcohol: whilst the sulphates themselves, with the exception of those of nickel and copper, experience no change beyond the loss of their water of crystallization. Both iodide and bromide of cadmium, and the chlorides of cobalt, cadmium, manganese, and copper, under similar circumstances effect the etherification of alcohol, but undergo no change themselves. With protochlorides of tin and of copper, the production of ether is sufficient to furnish a considerable stratum of ether, but a certain amount of permanent gas is also formed. Chloride of mercury blackens the alcohol, ether is formed, and much gas is liberated. Chlorides of zinc and ammonium effect a similar change;

the chlorides of aluminum, antimony, and perchloride of iron, yield a mixture of ether and hydrochloric ether.

It is obvious that these bodies act in some manner as yet unexplained, upon the alcohol, in consequence of which the latter becomes more or less completely resolved into ether and water. This effect cannot be produced by the mere action of heat alone; and it must be admitted, that the theory of etherification is still incomplete notwithstanding the numerous researches of which it has been the subject.

The oxygen in ordinary ether may be displaced by other bodies analogous to it, such as sulphur, selenium, and tellurium, as well as by chlorine, bromine, and iodine. The compounds thus formed are sometimes described under the names of hydrosulphuric, hydrochloric, hydrobromic, and hydriodic ethers.

(991) The following table exhibits the composition of a few of the principal compound ethylic ethers. It would be useless to attempt to enumerate them all, since every acid forms at least one ether, and some, such as the silicic and boracic, furnish more than one:—

		Boiling Point °F.	Specific Gravity.	
			Liquid.	Vapour.
Ethyl. . . .	$=(C_4H_5)$			
Oxide . . .	C_4H_5O, C_4H_5O	94·8	0·7365*	2·586
Sulphide . .	C_4H_5S, C_4H_5S	163·4	0·825	3·1
Bisulphide . .	$C_4H_5S_2, C_4H_5S_2$	304·0	1·0	4·27
Chloride . . .	C_4H_5Cl	51·9	0·921*	2·219
Bromide . . .	C_4H_5Br	105·8	1·4733*	3·754
Iodide . . .	C_4H_5I	158·5	1·9755*	5·475
Cyanide . . .	C_4H_5, C_2N	179·6	0·787	
Sulphate . .	$2\ C_4H_5O, S_2O_6$		1·120	
Sulphite . . .	$2\ C_4H_5O, S_2O_4$	320	1·1063*	4·78
Nitrate . . .	C_4H_5O, NO_5	185	1·112	
Nitrite . . .	C_4H_5O, NO_3	62	0·947	2·627
Phosphate . .	$3\ C_4H_5O, PO_5$	214		
Carbonate . .	$2\ C_4H_5O, C_2O_4$	257	0·965	4·09
Borate . . .	$3\ C_4H_5O, BO_3$	246	0·8849*	5·31
Bisilicate . .	$2\,(2\ C_4H_5O, SiO_2)$	330	0·933	7·32
Silicate . . .	C_4H_5O, SiO_2	608	1·079	
Formiate . .	C_4H_5O, C_2HO_3	127·7	0·9357*	2·573
Acetate . . .	$C_4H_5O, C_4H_3O_3$	164·9	0·9069*	3·067
Butyrate . .	$C_4H_5O, C_8H_7O_3$	238·8	0·9041*	4·04
Valerate . . .	$C_4H_5O, C_{10}H_9O_3$	272·3	0·894	4·558
Cyanate . . .	C_4H_5O, C_2NO	140	0·8981	2·475
Cyanurate . .	$3\ C_4H_5O, C_6N_3O_3$	529		7·4
Benzoate . .	$C_4H_5O, C_{14}H_5O_3$	408·2	1·053	5·407
Oxalate . . .	$2\ C_4H_5O, C_4O_6$	363·2	1·0229	5·087
Succinate . .	$2\ C_4H_5O, C_8H_4O_6$	419·0		6·06

* The numbers indicating the specific gravity, to which an asterisk is affixed, were taken at 32° F.

(*b*) *Hydracid Ethylic Ethers.*

(992) ***Hydrochloric Ether; Chloride of Ethyl*** (C_4H_5Cl), ***Sp. gr. of vapour*** 2·219, ***of liquid*** at 32°, 0·921.—This compound is obtained easily by distilling a mixture of 3 parts of oil of vitriol, 2 of alcohol, and four of fused chloride of sodium; the retort is connected with a tubulated receiver surrounded by water of a temperature of about 70°, where most of the alcohol and water which pass over during the operation are condensed, while the ether escapes in the form of vapour through a bent tube inserted into the tubulure of the receiver, and passing to the bottom of a flask kept cool with ice. The liquid which is thus condensed must be rectified from chloride of calcium. It then presents itself as a colourless liquid, of a penetrating, ethereal, and somewhat alliaceous odour. It boils at 51°·9; is slightly soluble in water, and burns with a brilliant flame edged with green, emitting fumes of hydrochloric acid. If passed through red-hot tubes, it is decomposed into equal measures of hydrochloric acid and olefiant gas; $C_4H_4 + HCl$. It is sparingly soluble in water, but is freely dissolved by alcohol. These solutions give no precipitate with nitrate of silver. If an alcoholic solution of potash be enclosed in a sealed tube with hydrochloric ether and heated to 212°, chloride of potassium and ordinary ether are formed; $C_4H_5Cl + KO = C_4H_5O + KCl$: but if the vapour of the ether be passed over heated hydrate of potash, water and pure olefiant gas are evolved; $C_4H_5Cl + KO, HO = C_4H_4 + 2\ HO + KCl$.

(993) ***Hydrobromic Ether: Bromide of Ethyl*** (C_4H_5Br), ***Sp. gr. of liquid*** 1·4733 at 32°, ***of vapour*** 3·754.—This compound is usually prepared by adding by degrees 7 or 8 parts of bromine to 40 parts of alcohol (sp. gr. 0·827) and 1 part of phosphorus, contained in a retort: the reaction of bromine and phosphorus upon each other in the presence of the water contained in the alcohol produces hydrobromic acid and phosphorous acid; and on subjecting the mixture to distillation, hydrobromic ether comes over. It may be purified by agitation with a weak solution of potash, after which it is left to subside; it is then decanted and redistilled.

Bromide of ethyl is a colourless liquid of a peculiar ethereal odour and taste. It boils at 105°·8, though it requires to be heated to 120° before ebullition commences. It remains liquid at —24°. It burns with difficulty, producing a green flame and emitting fumes of hydrobromic acid.

(994) *Hydriodic Ether: Iodide of Ethyl* (C_4H_5I), *Sp. gr. of liquid* at 32°, 1·9755, *of vapour* 5·475.—In order to prepare this ether, 100 parts of alcohol are placed in a retort, and a small amount of iodine is introduced; phosphorus is added in small quantities at a time until the liquid becomes colourless; a fresh portion of iodine is then added, and then a fresh quantity of phosphorus; this may be continued until about 60 parts of iodine and 20 parts of phosphorus have been added. The mixture thus obtained is then cautiously distilled, taking care that the iodine (as shown by its brown colour) is in slight excess. The iodide of phosphorus, which is formed during this operation, is decomposed into phosphorous and hydriodic acids, and the latter, reacting upon the alcohol, liberates hydriodic ether and water—

$$C_4H_5O,\ HO + HI = C_4H_5I + 2\ HO.$$

Iodide of ethyl is a colourless liquid, which, if kept in half-closed bottles, soon undergoes a partial decomposition, and becomes brown from the liberation of iodine. It boils at 158°·5. When heated with water to 300°, in a sealed tube, it becomes decomposed into ordinary ether and hydriodic acid (Frankland); according to Hofmann, if boiled with water and oxide of silver, alcohol and iodide of silver are produced;—

$$C_4H_5I + AgO + HO = C_4H_5O,\ HO + AgI;$$

and Wurtz finds that when the anhydrous iodide is heated in a sealed tube with oxide of silver, iodide of silver and ordinary ether are formed with facility.

Both the bromide and the iodide of ethyl have been extensively employed for the preparation of substitution compounds containing ethyl; and it was by decomposing iodide of ethyl in a sealed tube by means of zinc that Frankland succeeded in isolating the hydrocarbon, which he regards as ethyl.

(995) SULPHIDES OF ETHYL.—Alcohol furnishes not less than three remarkable compounds which contain sulphur. One of these ($C_4H_5S,\ C_4H_5S$) corresponds in composition to the oxide, or ordinary ether; the second is the *bisulphide of ethyl* ($C_4H_5S_2,\ C_4H_5S_2$)—no oxidized representative of this body is known; and the third is *mercaptan* ($C_4H_5S,\ HS$), a compound which corresponds with alcohol in which the oxygen is displaced by sulphur. All these bodies are distinguished by a disgusting alliaceous odour which is extremely powerful and persistent.

Hydrosulphuric Ether: Sulphide of Ethyl ($C_4H_5S,\ C_4H_5S$), *Sp. gr. of liquid* 0·825, *of vapour* 3·1.—This compound is easily prepared by decomposing an alcoholic solution of protosulphide of potassium (469), by transmitting into it the vapour of chloride of ethyl and submitting it to distillation: the distilled liquid is to be well washed with water and rectified from chloride of calcium. It is a colourless liquid of an intensely powerful odour of garlic. It boils at $163^{\circ}\cdot4$, and forms crystalline compounds with some of the metallic chlorides; its compound with corrosive sublimate contains (C_4H_5S, $HgCl$).

Bisulphide of ethyl ($C_4H_5S_2$, $C_4H_5S_2$) boils at $303^{\circ}\cdot8$, emitting a vapour of sp. gr. 4·27. It is obtained by distilling 3 parts of sulphethylate of potash dissolved in its own weight of water with 2 parts of pentasulphide of potassium. The alcoholic solution of this compound gives a yellow precipitate with acetate of lead, and a white with corrosive sublimate. There appears ground for supposing that higher sulphides of ethyl may be obtained.

Mercaptan (C_4H_5S, HS), *Sp. gr. of liquid* 0·835, *of vapour* 2·14.—This compound may be obtained by distilling a mixture of equal parts of an aqueous solution of sulphethylate of lime, of sp. gr. 1·28, and of a solution of potash of the same density, previously saturated by sulphuretted hydrogen:—

$$\overbrace{KO,\ C_4H_5O,\ S_2O_6}^{\text{Sulphethylate of Potash.}} + \overbrace{KS,\ HS}^{\text{Hydrosulph. Potass.}} = \overbrace{C_4H_5S,\ HS}^{\text{Mercaptan.}} + \overbrace{2\ (KO,\ SO_3)}^{\text{Sulph. Potash.}}.$$

A better plan, according to Regnault, is to saturate an alcoholic solution of potash completely with sulphuretted hydrogen, and then to distil it with hydrochloric ether. Mercaptan is a colourless, transparent, very mobile liquid, with a most intense and repulsive odour of garlic; it boils at 97°, is very inflammable, and burns with a blue flame. It is sparingly soluble in water, but is dissolved freely by alcohol and ether. The solution is neutral to test papers, but mercaptan nevertheless presents the characters of a feeble acid. It dissolves sulphur, phosphorus, and iodine, with facility. Mercaptan becomes solid at —8°. If a glass rod be moistened with this compound and moved quickly through the air, the cold produced by the evaporation is sufficient to freeze a portion of the remainder. Mercaptan forms with the metals compounds which correspond to the hydrosulphates, but they contain ethyl instead of hydrogen, as may be seen by comparing their respective formulæ; thus—

$$\overbrace{KS,\ (C_4H_5)\ S}^{\text{Mercaptide of Potassium.}} \quad ; \quad \overbrace{KS,\ (H)\ S}^{\text{Hydrosulphate of Potassium.}}.$$

Mercaptide of potassium is obtained by acting on pure mercaptan with potassium, hydrogen gas being liberated: but it is more particularly on the oxides of the noble metals that the action of mercaptan is remarkable. The mercaptide of mercury (HgS, C_4H_5S) is a white crystalline compound destitute of odour, and fusible at 185°. It is insoluble in water, but soluble in alcohol: it is easily obtained by digesting oxide of mercury in an alcoholic solution of mercaptan, water being formed, whilst the odour of mercaptan disappears:—

$$HS, C_4H_5S + HgO = HgS, C_4H_5S + HO.$$

The corresponding compound of gold is white and gelatinous; that of platinum is bright yellow, and that of lead (PbS, C_4H_5S) is yellow and crystalline.

(996) Selenium and tellurium each form compounds with ethyl, corresponding to the sulphide of ethyl; they may be obtained by distilling selenide or telluride of potassium with sulphethylate of potash. It is, however, to be remarked that both the selenide and the telluride of ethyl combine with chlorine, bromine, and iodine; and they become oxidized, and form salts with the oxyacids just as though they were metallic bodies. In fact, they present many chemical analogies with the compounds which arsenic, antimony, bismuth, and other metals form with ethyl (1033).

A compound of selenide of ethyl and seleniuretted hydrogen (SeH, C_4H_5Se), corresponding in composition and properties to mercaptan, is formed during the operation of preparing the selenide of ethyl.

(997) *Cyanide of Ethyl: Hydrocyanic Ether: Propionitrile* ($C_4H_5Cy = C_6H_5N$), *Sp. gr. of liquid* 0·787.—This compound is obtained in a manner analogous to the foregoing, by the distillation of sulphethylate of potash with cyanide of potassium. It is a colourless, very poisonous liquid, of an alliaceous odour. It boils at 179°·6, and emits an inflammable vapour. When cyanide of ethyl is treated with a boiling solution of potash, the elements of water are assimilated, ammonia is evolved, and propionate of potash is formed:—

$$\overbrace{C_4H_5, C_2N}^{\text{Cyanide of Ethyl.}} + KO, HO + 2\ HO = \overbrace{KO, C_6H_5O_3}^{\text{Propionate of Potash.}} + H_3N.$$

A similar mode of decomposition is observed to occur with all the hydrocyanic ethers when treated with hydrate of potash: they all combine with the elements of water and yield one of the acids homologous with formic acid; cyanide of methyl thus yields acetate of potash:—

$$\overbrace{C_2H_3, C_2N}^{\text{Cyanide of Methyl.}} + KO, HO + 2\,HO = \overbrace{(KO, C_4H_3O_3)}^{\text{Acetate of Potash.}} + H_3N;$$

and cyanide of amyl in like manner furnishes caproate of potash;

$$\overbrace{C_{10}H_{11}, C_2N}^{\text{Cyanide of Amyl.}} + KO, HO + 2\,HO = \overbrace{KO, C_{12}H_{11}O_3}^{\text{Caproate of Potash.}} + H_3N.$$

The hydrocyanic ethers (the *nitriles* of some chemists), as a class, may also be obtained by a process of dehydration, from the acids to which they correspond; that is to say, if the ammoniacal salts of the acids homologous with the formic, be distilled with anhydrous phosphoric acid, or be otherwise treated in such a manner as to deprive them of 4 equivalents of water, they yield one of the hydrocyanic ethers, thus:—

$$\overbrace{H_4NO, C_2H\,O_3}^{\text{Formiate of Ammonia.}} - 4\,HO = \overbrace{H, C_2N}^{\text{Hydrocyanic Acid.}} = (C_2H\,N, \text{ Formio-nitrile.})$$

$$\overbrace{H_4NO, C_4H_3O_3}^{\text{Acetate of Ammonia.}} - 4\,HO = \overbrace{C_2H_3, C_2N}^{\text{Cyanide of Methyl.}} = (C_4H_3N, \text{ Acetonitrile.})$$

$$\overbrace{H_4NO, C_6H_5O_3}^{\text{Propionate of Ammonia.}} - 4\,HO = \overbrace{C_4H_5, C_2N}^{\text{Cyanide of Ethyl.}} = (C_6H_5N, \text{ Propionitrile.})$$

and in this manner the hydrocyanic ethers of several series of alcohols have been obtained, although the corresponding alcohols are at present unknown (1046, 1055).

The action of potassium upon hydrocyanic ether is remarkable. If the ether be allowed to fall drop by drop upon potassium contained in a flask fitted to a vertical condenser, by means of which any part of the ether which escapes decomposition is allowed to fall back upon the potassium, hydride of ethyl (C_4H_5H) is formed, whilst cyanide of potassium is produced, and an alkaline base termed *cyanethine* ($C_{18}H_{15}N_3$) remains in the retort (Frankland and Kolbe). This substance is polymeric with hydrocyanic ether. It crystallizes from boiling water in pearly scales, and forms salts with the acids. The nitrate ($C_{18}H_{15}N_3$, HO, NO_5) crystallizes in large colourless prisms which are neutral in their reactions. The other hydrocyanic ethers when treated with potassium appear to furnish compounds analogous to cyanethine.

(c) *Ethylic Ethers of the Oxyacids.*

(998) *Sulphate of Ethyl,* or true *Sulphuric Ether* ($2\,C_4H_5O$, S_2O_6), *Sp. gr. liquid* 1·120.—This compound was recently discovered by Wetherill. It is obtained by the direct combination of

ether with sulphuric anhydride. The vapours of the anhydrous acid are transmitted into a flask containing ether, which is kept cool by ice; the syrupy liquid thus produced is agitated with its own volume of ether, and with four times its bulk of water; when left at rest the sulphate of ethyl rises to the surface; it is purified by agitation with milk of lime, washed, filtered, and dried *in vacuo*. Sulphuric ether is an oily liquid, of a burning taste and ethereal odour, resembling that of peppermint. It is scarcely possible to distil it without occasioning its decomposition, as a temperature of 270° or 290° resolves it into alcohol, sulphurous acid, and olefiant gas.

Sweet or *heavy oil of wine* appears to be a mixture of the foregoing compound with some hydrocarbons polymeric with olefiant gas; it is obtained during the later stages of the distillation of ether. If this oil be treated with a solution of potash, it is decomposed; sulphethylate of potash, and a hydrocarbon, termed *etherole* ($C_{32}H_{32}$?) rises to the surface. This compound, known also as *light oil of wine*, is polymeric with olefiant gas, and forms a colourless liquid which has a sp. gr. of 0·917; it boils at 536°, and is readily soluble in ether and absolute alcohol. When exposed to a temperature of −30°, it usually deposits semitransparent, friable, colourless prisms of an isomeric hydrocarbon named *etherin;* these fuse at 230°, and boil at 500°; they are lighter than water, in which they are insoluble, but are dissolved freely by alcohol and ether.

(999) *Nitric Ether* (C_4H_5O, NO_5), *Sp. gr. of liquid* 1·112.—Millon obtains this substance by gently heating a mixture of 1 volume of nitric acid, of sp. gr. 1·40 (to which a few grains of nitrate of urea have been added to prevent the formation of nitrous acid), and 2 volumes of alcohol, of sp. gr. 0·842; under these circumstances the operation proceeds quietly. The first portions of the distillate contain little except alcohol, but as soon as the liquid which distils over becomes turbid on the addition of water, the receiver must be changed and the nitric ether collected separately: the distillation must not be carried too far, otherwise it becomes mixed with secondary products, which are removed with difficulty. The ether is purified by agitation with a weak solution of alkali, and rectified from chloride of calcium. Nitric ether is a colourless liquid of an agreeable odour, and a taste at first very sweet, but followed by a bitterish after taste. The boiling point of this ether is 185°. Its vapour burns with a white luminous flame, and if heated a little beyond its boiling point, it is decomposed with explosion.

Nitrous Ether (C_4H_5O, NO_3), *Sp. gr. of liquid* 0·947, *of vapour* 2·627.—This ether has long been used in solution in alcohol as a therapeutic agent, which forms the *Spiritus Etheris Nitrosi* of the London Pharmacopœia. The safest method of preparing it consists in introducing into a retort containing copper filings, 1 measure of alcohol (sp. gr. 0·83), to which 1 measure of nitric acid of sp. gr. 1·36 is gradually added. The reaction of nitric acid upon alcohol begins at a very moderate heat, and is apt to become extremely violent, therefore no external heat should be applied during the distillation, after the reaction has once commenced. The vapours which are evolved should be transmitted through a washing bottle containing water, then through a long bent tube filled with chloride of calcium, and finally should be condensed in a flask cooled by ice. Nitrous ether is of a pale yellow colour, and an agreeable odour of apples. It boils at 61°·5 (Liebig). When this ether is kept in contact with water, it speedily becomes acid, and it is remarkable that the acid which is formed is the malic (Berzelius). A solution of the protosulphate of iron becomes blackened when mixed with nitrous ether.

Nitrous ether is decomposed by transmitting its vapour through a red-hot tube, giving rise to a variety of products, among which are hydrocyanate and carbonate of ammonia, derived from the reactions of the nitrogen upon the carbon and hydrogen.

(1000) *Perchloric Ether* (C_4H_5O, ClO_7).—This singular compound cannot be prepared without considerable danger, as it explodes with extraordinary violence when heated a little beyond 212°, and a similar result is produced by friction or by a sudden blow. In order to obtain it, a few grains of crystallized sulphethylate of baryta are placed in a tube retort with an equal weight of perchlorate of baryta, and are cautiously distilled by the heat of an oil bath. The ether is heavier than water, and has a sweetish pungent taste, somewhat resembling that of cinnamon. Its boiling point is not known with accuracy, but it is above 212°. The explosive character of the compound depends upon the large proportion of oxygen which it contains in union with chlorine, for which the affinity of oxygen is very small, whilst hydrogen has a powerful affinity for both chlorine and oxygen; the oxygen is sufficient to convert the carbon into the form of carbonic oxide, and the hydrogen into water, $C_4H_5O, ClO_7 = 4\ CO + 4\ HO + HCl$.

(1001) SILICIC ETHERS.—Few of the ethers are more remarkable than those obtained by Ebelmen with silicic acid. In these compounds the polybasic character of the acid is preserved.

Disilicate of Ethyl [$2(2\ C_4H_5O,SiO_2)$], *Sp. gr. of liquid* 0·933, *of vapour* 7·32.—When absolute alcohol is gradually added to chloride of silicon, a powerful reaction occurs; hydrochloric acid is evolved in abundance, and a colourless liquid is obtained, which when submitted to distillation at first evolves hydrochloric acid, but the boiling point rises rapidly until it reaches 330,° at which temperature pure silicic ether distils over. It is a limpid liquid, of a pleasant ethereal odour, and a hot taste resembling that of pepper. It is combustible, and burns with a flame of dazzling whiteness, depositing pulverulent silica. The composition of this body is remarkable, 4 volumes of vapour being produced from the compound, $C_{16}H_{20}Si_2O_8$. This ether is not miscible with water, but is decomposed by it with the separation of gelatinous hydrate of silica. If this decomposition be allowed to take place slowly, by placing an imperfectly closed vessel containing the ether in a moist atmosphere, the silica is gradually deposited in the form of a hard transparent solid, resembling quartz in appearance.

Silicic Ether ($C_4H_5O,\ SiO_2$).—A second ether containing only half the quantity of oxide of ethyl that is present in the foregoing, may be procured by acting upon alcohol of sp. gr. 0·838, with chloride of silicon, and distilling; the disilicate is formed at the same time, and the first portions of the distillate consist entirely of this compound; but by degrees the boiling point becomes higher, and when it reaches 660°, the pure monosilicate passes over. The disilicate of ethyl is in fact transformed into the monobasic silicate by the action of the water present in the dilute alcohol; water occasioning the decomposition of the disilicate into the monosilicate, whilst alcohol is set free—

$$2\ \overbrace{C_4H_5O,\ SiO_2}^{\text{Disilicate of Ethyl.}} + HO = \overbrace{C_4H_5O,\ SiO_2}^{\text{Monosilicate of Ethyl.}} + \overbrace{C_4H_5O,\ HO.}^{\text{Alcohol.}}$$

If more water be added, a viscous compound is obtained, which, according to Ebelmen, contains a third ether, with twice as much silicic acid as the foregoing one.

Terchloride of boron yields with anhydrous alcohol a *tribasic boracic ether* ($3\ C_4H_5O,\ BO_3$), which is immediately decomposed by water. It has a sp. gr. of 0·8849; and it boils at 246°. Boracic acid is readily soluble in anhydrous alcohol with evolution of heat; Ebelmen considers that under these circumstances a second ether is formed, which when pure is solid at ordinary temperatures. It softens at about 100°, and can be drawn out into long threads.

Its composition is not certainly known, but it has been represented as (C_4H_5O, 2 BO_3), analogous to ordinary borax.

(1002) *Formic Ether* (C_4H_5O, C_2HO_3), *Sp. gr. of liquid* 0·915 at 64°, *of vapour* 2·573.—This ether is readily obtained by distilling 7 parts of dry formiate of soda with 10 of oil of vitriol, and 9 of alcohol of sp. gr. 0·825. Wöhler prepares it from a mixture of 10 parts of starch, with 37 of finely powdered binoxide of manganese, and 15 parts of alcohol, 15 of water, and 30 of oil of vitriol: the whole is distilled by a gentle heat in a capacious retort. The formic acid generated by the oxidation of the starch, reacts upon the alcohol at the moment of its formation. Formic ether does not mix with the water which accompanies it; and is purified by washing with water, and rectification from chloride of calcium. Formic ether is also a secondary product of the reaction of nitric acid upon alcohol. When pure it has an agreeable odour and taste, recalling that of peach kernels. It is colourless, and boils at 127°·7. In contact with water it becomes readily resolved into formic acid and alcohol.

(1003) *Acetic Ether* (C_4H_5O, $C_4H_3O_3$), *Sp. gr. of liquid* 0·89, *of vapour* 3·06.—Acetic acid, if repeatedly distilled with alcohol, gives rise to the formation of acetic ether, but the effect is much hastened by the addition of sulphuric acid to the liquid. A mixture of 6 parts of alcohol, 4 of acetic acid, and 1 part of oil of vitriol, yields the ether with facility. When a volume of liquid equal to that of the alcohol employed, has come over, the process is stopped; the distillate is washed twice with its own bulk of water, and rectified from chloride of calcium. Acetate of soda or acetate of lead may be substituted for acetic acid in the foregoing process, but then a larger quantity of oil of vitriol is needed. If 6 parts of alcohol be employed, 100 of acetate of soda and 15 of oil of vitriol may be used; or 24 parts of acetate of lead (dried), and 9 of oil of vitriol.

Acetic ether has an agreeable odour, remotely resembling that of apples, and a burning taste; a small quantity of it appears to be contained in several varieties of wine. Water dissolves about one-seventh of its bulk of it. Acetic ether is a good solvent for the essential oils, for the resins, and for pyroxylin. It boils at 165°. A mixture of this ether with an alcoholic solution of hydrate of potash, is immediately decomposed into acetate of potash and alcohol. Acetic ether dissolves chloride of calcium readily, and forms with it a crystallizable compound, which yields the ether unchanged on the application of heat.

(1004) *Œnanthic Ether* (C_4H_5O, $C_{14}H_{13}O_2$?), *Sp. gr. of liquid* 0·862, *of vapour* 10·477.—Delffs regards this body as pelargonic ether, C_4H_5O, $C_{18}H_{17}O_3$, and the analyses of Liebig and Pelouze are not inconsistent with this view. This ether is a fragrant liquid of a stupifying, extremely powerful odour, which is the cause of the peculiar smell that characterizes grape wine, and which adheres so tenaciously to vessels in which wine has been kept. When large quantities of wine, or the lees of wine, are distilled, this ether passes over, mixed with free œnanthic acid, in the form of an oily layer; the crude product is gently heated with a solution of carbonate of soda, which removes the free acid, whilst the ether floats as an oily layer upon the surface. When pure it boils at 446°, and emits a very dense and highly inflammable vapour. The quantity of this ether appears to increase with the age of the wine. Œnanthic (probably pelargonic) acid may be obtained by decomposing the ether with potash, and distilling the œnanthate of potash with sulphuric acid. It is a semi-solid fat, which, according to Liebig and Pelouze, contains one equivalent of oxygen less than œnanthylic acid, but this requires confirmation.

(1005) *Oxalic Ether* ($2\ C_4H_5O, C_4O_6$), *Sp. gr. of liquid* 1·0229, *of vapour* 5·087.—This is one of the most interesting of the numerous ethers which are formed with the organic acids. It is obtained by distilling rapidly a mixture of 4 parts of alcohol (sp. gr. 0·825), 5 of oil of vitriol, and 4 of binoxalate of potash. The distillate should be washed with water, and rectified from litharge to retain any traces of free oxalic acid. Oxalic ether is heavier than water. It is colourless, and has an agreeable ethereal odour and taste. It boils at 364°. If pure it may be kept unchanged in contact with water, but if it retain any acid it is slowly decomposed into oxalic acid and alcohol; an excess of hydrate of potash decomposes it into oxalate of potash and alcohol with rapidity; but if the quantity of potash be small, alcohol and oxalethylate of potash are formed; the reaction in the first case being:—

$$\overbrace{2\ C_4H_5O, C_4O_6}^{\text{Oxalic Ether.}} + 2\,(KO, HO) = \overbrace{2\ KO, C_4O_6}^{\text{Oxalate of Potash.}} + \overbrace{2\,(C_4H_5O, HO)}^{\text{Alcohol.}}$$

and in the second case:—

$$\overbrace{2\ C_4H_5O, C_4O_6}^{\text{Oxalic Ether.}} + KO, HO = \overbrace{KO, C_4H_5O, C_4O_6}^{\text{Oxalethylate of Potash.}} + \overbrace{C_4H_5O, HO}^{\text{Alcohol.}}$$

When an alcoholic solution of ammonia is added to oxalic ether, a somewhat analogous decomposition is effected, an excess of ammonia giving rise to the formation of oxamide and alcohol:—

$$\overbrace{2\,C_4H_5O,\,C_4O_6}^{\text{Oxalic Ether.}} + \overbrace{2\,(H_3N)}^{\text{Ammonia.}} = \overbrace{(2\,H_2N,\,C_4O_4)}^{\text{Oxamide.}} + \overbrace{2\,(C_4HO,\,H_5O)}^{\text{Alcohol.}}$$

This reaction furnishes one of the best methods of procuring oxamide. If the ether be in excess the decomposition is different; alcohol, and a substance soluble in alcohol but insoluble in water, crystallizing in beautiful pearly tables, is formed: this body was originally termed *oxamethane*, but it is now admitted to be *oxamic ether*, or the ether of amidated oxalic acid ($HO,\,H_2NC_4O_5$; 1058):—

$$\overbrace{2\,C_4H_5O,\,C_4O_6}^{\text{Oxalic Ether.}} + H_3N = \overbrace{C_4H_5O,\,H_2NC_4O_6}^{\text{Oxamic Ether.}} + \overbrace{C_4H_5O,\,HO}^{\text{Alcohol.}}$$

If equal parts of oxalethylate of potash and sulphomethylate of this base be thoroughly dried, then mixed and submitted to distillation, a curious double ether (*methyl-ethyloxalic ether*, ($C_2H_3O,\,C_4H_5O,\,C_4O_6$) is obtained. It forms a yellowish oil, heavier than water, of sp. gr. 1·127, boiling at about 330°, and emitting a vapour of sp. gr. 4·67.

(1006) *Carbonic Ether* ($2\,C_4H_5O,C_2O_4$), *Sp. gr.* 0·965, *of vapour* 4·09.—This ether cannot be obtained by the ordinary mode of preparing these compounds. It may be formed by heating carbonate of silver with iodide of ethyl in a closed tube; but it is generally procured by heating sodium or potassium with oxalic ether, in which case carbonic oxide is disengaged abundantly, whilst carbonic ether distils over, and oxalate of the alkali remains in the retort. Carbonic ether is a very mobile liquid, of a sweet aromatic odour; it is not very inflammable, but is readily decomposed by an alcoholic solution of potash. When heated in a sealed tube with an alcoholic solution of ammonia, alcohol and carbamic ether (urethane) are formed; and if the temperature be raised to about 356°, the excess of ammonia slowly converts the carbonic ether into alcohol and urea, or carbamide (Natanson); both decompositions being analogous to those which oxalic ether undergoes with greater facility by the same reagents:—

$$\overbrace{2\,C_4H_5O,\,C_2O_4}^{\text{Carbonic Ether.}} + H_3N = \overbrace{C_4H_5O,\,H_2NC_2O_3}^{\text{Carbamic Ether.}} + \overbrace{C_4H_5O,\,HO}^{\text{Alcohol.}}$$

$$\overbrace{C_4H_5O,\,H_2NC_2O_3}^{\text{Carbamic Ether.}} + H_3N = \overbrace{H_4N_2C_2O_2}^{\text{Carbamide (Urea.)}} + \overbrace{C_4H_5O,\,HO}^{\text{Alcohol.}}$$

Urethane, or *carbamic ether,* is a substance which resembles spermaceti in appearance; it evinces a remarkable disposition to crystallize, and forms large transparent leaflets, fusible below 212°. It boils at 356°, and yields a vapour of sp. gr. 3·14. It is very soluble in alcohol and ether. If distilled in a moist state, it gives off large quantities of ammonia.

Chlorocarbonic Ether (C_4H_5O, C_2ClO_3), *Sp. gr. of liquid* 1·139, *of vapour* 3·823.—This compound is obtained by absorbing phosgene gas by absolute alcohol, and rectifying the product from powdered litharge and chloride of calcium. It is a colourless, very limpid liquid, which emits a suffocating odour, and irritates the eyes powerfully. It boils at 201°, emitting an inflammable vapour, which burns with a green flame. It is not soluble in cold water, but is decomposed by boiling water. Gerhardt represents this compound as an oxychloride, which bears the same relation to carbethylic acid that benzoic oxychloride (chloride of benzoyl) does to benzoic acid:—

$$\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\H\end{matrix}\right\}O_2}^{\text{Benzoic Acid.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_4H_5, C_2O_4\\H\end{matrix}\right\}O_2}^{\text{Carbethylic Acid.}}$$

$$\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\Cl\end{matrix}\right\}}^{\text{Benzoic Oxychloride.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_4H_5, C_2O_4\\Cl\end{matrix}\right\}}^{\text{Chlorocarbonic Ether.}}$$

(1007) *Cyanic Ether* (C_4H_5O, C_2NO), *Sp. gr. of liquid* 0·898, *of vapour* 2·475.—This ether may be prepared by distilling cyanate of potash with the sulphethylate of that base. It is an extremely pungent volatile liquid of high refracting power. Cyanic ether when decomposed by hydrate of potash undergoes a remarkable transformation, in consequence of which it is converted into a new base, ethylia, C_4H_7N ($= \left.\begin{matrix}C_4H_5\\H\\H\end{matrix}\right\}N$), which corresponds to ammonia in which one equivalent of hydrogen has been displaced by ethyl (C_4H_5) the organic radicle of ether. (Wurtz, *Ann. de Chimie,* III., xxx., 447.)

$$\overbrace{C_4H_5O, C_2NO}^{\text{Cyanic Ether.}} + \overbrace{2\,(KO, HO)}^{\text{Hydrate of Potash.}} = \overbrace{2\,(KO, CO_2)}^{\text{Carbonate of Potash.}} + \overbrace{C_4H_5, H_2N}^{\text{Ethylia.}}.$$

A similar decomposition ensues when the cyanic ethers of the other alcohols are treated with hydrate of potash, a series of alkalies homologous with ethylia being formed. Thus, starting with hydrated cyanic acid, which contains hydrogen instead of one of the radicles of the ethers :—

$$\overbrace{H\ O, C_2NO}^{\text{Cyanic Acid.}} + 2\,(KO, HO) = 2\,(KO, CO_2) + \overbrace{H, H_2N}^{\text{Ammonia.}}$$

$$\overbrace{C_2H_3O, C_2NO}^{\text{Methyl-cyanic Ether.}} + 2\,(KO, HO) = 2\,(KO, CO_2) + \overbrace{C_2H_3, H_2N}^{\text{Methylia.}}$$

$$\overbrace{C_{10}H_{11}O, C_2NO}^{\text{Amyl-cyanic Ether.}} + 2\,(KO, HO) = 2\,(KO, CO_2) + \overbrace{C_{10}H_{11}, H_2N}^{\text{Amylia.}}$$

When cyanic ether is treated with ammonia, combination occurs between the two bodies, and a body homologous with urea, *ethyl-urea* ($C_6H_8N_2O_2$), is formed :—

$$\overbrace{C_4H_5O, C_2NO}^{\text{Cyanic Ether.}} + H_3N = \overbrace{H_3(C_4H_5)N_2C_2O_2}^{\text{Ethyl-urea.}}.$$

The other cyanic ethers, when treated with ammonia, form homologous bodies, or ureas in which the place of one equivalent of hydrogen has been supplied by one equivalent of the various radicles of the ethers. Thus :—

Ordinary urea . = $H_3(\ H\ )N_2C_2O_2$ } from hydrated cyanic acid and ammonia.
Methyl-urea . . = $H_3(C_2H_3)N_2C_2O_2$ } from methylcyanic ether and ammonia.
Ethyl-urea . . = $H_3(C_4H_5)N_2C_2O_2$ from ethylcyanic ether.
Amyl-urea . . = $H_3(C_{10}H_{11})N_2C_2O_2$ from amylcyanic ether.

The various cyanic ethers when placed in contact with water undergo decomposition; they evolve carbonic acid, and the members of another series of ureas are produced, in which two equivalents of the hydrogen contained in ordinary urea are displaced by two equivalents of the alcohol radicle; for example :—

$$2\overbrace{C_4H_5O, C_2NO}^{\text{Cyanic Ether.}} + 2\,HO = 2\,(CO_2) + \overbrace{H_2(C_4H_5)_2N_2C_2O_2}^{\text{Diethyl-urea.}}$$

Methyl-cyanic ether yields under like circumstances dimethyl-urea;

$$2\overbrace{C_2H_3O, C_2NO}^{\text{Methyl-cyanic Ether.}} + 2\,HO = 2\,(CO_2) + \overbrace{H_2(C_2H_3)_2N_2C_2O_2}^{\text{Dimethyl-urea.}};$$

and amyl-cyanic ether yields diamyl-urea;

$$2\overbrace{C_{10}H_{11}O, C_2NO}^{\text{Amyl-cyanic Ether.}} + 2\,HO = 2\,(CO_2) + \overbrace{H_2(C_{10}H_{11})_2N_2C_2O_2}^{\text{Diamyl-urea.}}.$$

It may be observed that dimethyl-urea is isomeric with ethyl-urea; for

$$\overbrace{H_2(C_2H_3)_2N_2C_2O_2}^{\text{Dimethyl-urea.}} = C_6H_8N_2O_2 = \overbrace{H_3(C_4H_5)N_2C_2O_2}^{\text{Ethyl-urea.}}.$$

Methyl-cyanic ether undergoes a singular spontaneous change even when sealed up in a tube; in consequence of which it, in the course of a few hours, becomes converted into a crystalline mass of methyl-cyanuric ether.

(1008) *Cyanuric Ether* (3 C_4H_5O, $C_6N_3O_3$), *Sp. gr. of vapour* 7·4.—This compound is obtained by distilling a mixture of sulphethylate, and cyanurate of potash, by the heat of an oil-bath. It is isomeric with cyanic ether: but it is solid at ordinary temperatures, and may be obtained from its solution in ether in brilliant crystals, which melt at 185°, forming a liquid heavier than water, which boils at 529°, and may be distilled unaltered. When treated with hydrate of potash, it yields ethylia. The cyanuric ethers of the other alcohols yield the corresponding alkalies when similarly treated, the products being identical with those which are furnished when the cyanic ethers of the same series are similarly decomposed:—

$$\overbrace{3\ C_4H_5O,\ C_6N_3O_3}^{\text{Cyanuric Ether.}} + 6\,(KO,\ HO) = 6\,(KO,\ CO_2) + 3\,\overbrace{(C_4H_5,\ H_2N)}^{\text{Ethylia.}}$$

Allophanic Ether (C_4H_5O, $C_4H_3N_2O_5$).—This compound was long mistaken for cyanuric ether. It is obtained by transmitting the vapours of hydrated cyanic acid into alcohol. It is a solid crystalline, colourless, tasteless, inodorous body which is insoluble in cold water, but is soluble in boiling water, in ether, and in boiling alcohol. It is soluble in cold baryta water, which converts it into alcohol, and a new salt, allophanate of baryta (BaO, $C_4H_3N_2O_5$). The acid is not known except in combination.

(*d*) *Ethers not derived from Ethylic Alcohol.*

(1009) Methylic Ether, or *Oxide of Methyl* (C_2H_3O, C_2H_3O), *Sp. gr. of vapour* 1·617.—By distilling 1 part of pyroxylic spirit and 4 parts of oil of vitriol, a colourless gas with a peculiar oppressive ethereal odour is disengaged, which is the homologue of ether in the ethylic series. It is accompanied by carbonic and sulphurous acids, which may be removed by allowing the gaseous mixture to stand for twenty-four hours in contact with slaked lime. Gaseous methylic ether is freely soluble in water, which dissolves about 37 times its bulk of the gas, and acquires its odour and pungent ethereal taste. It is still more soluble in alcohol. This gas is very inflammable, and burns with a pale flame; it is not liquefiable by a cold of 0° F. This substance, it should be observed, is isomeric with alcohol, with which it corresponds, both in its equivalent number and in the density of its vapour. Compounds of methyl may be obtained with chlorine, bromine, iodine, and sulphur, forming chloride, bromide, iodide, and sulphide of methyl: all these bodies are inflammable: the chloride is gaseous at ordinary temperatures; the bromide and the iodide are volatile liquids of considerable density. All these compounds are prepared like the corresponding compounds of ethyl. Combinations of oxide of methyl with the oxyacids also exist, forming a class of compounds parallel with the ethylic oxyacid ethers: thus we have sulphate, nitrate, oxalate, acetate of methyl, and so on.

(1010) *Methyl-Sulphuric Ether*, or *Sulphate of Methyl* ($2\ C_2H_3O, S_2O_6$), is procured by distilling 1 part of pyroxylic spirit with 8 or 10 parts of oil of vitriol; the ether passes over as a tasteless oily liquid, and collects in the receiver. It must be washed with cold water, digested on quicklime to free it from sulphurous acid and water, and then rectified. It is thus obtained as a colourless liquid which boils at 370°, and gives off a vapour containing 2 equivalents of oxide of methyl and 2 of sulphuric acid in 4 volumes. It is slowly decomposed by water in the cold, but is quickly resolved by it at the boiling point into wood spirit and sulphomethylic acid.

Methyl-Acetic Ether; Acetate of Methyl ($C_2H_3O, C_4H_3O_3$), is formed abundantly during the destructive distillation of wood, and enters largely into the composition of crude wood spirit. It is a colourless liquid, of an agreeable ethereal odour, boiling at 133°; it is freely soluble in water. The hydrated alkalies decompose it into acetic acid and wood spirit. It may be obtained by distilling 2 parts of wood spirit with 1 part of concentrated acetic acid, and 1 of oil of vitriol; the crude product is rectified from chloride of calcium, which retains the unchanged wood spirit.

Methyl-Oxalic Ether, or *Oxalate of Methyl* ($2\ C_2H_3O, C_2O_6$), at ordinary temperatures is solid, and may be sublimed without difficulty. A compound of oxide of methyl has in one instance been discovered ready formed in the vegetable kingdom, constituting, in combination with salicylic acid, *salicylate of methyl*, the essential oil procured from the *Betula lenta*, a species of birch, and from the *winter green* (*Gaultheria procumbens*) ($C_2H_3O, C_{14}H_5O_5$): a compound exactly resembling the natural oil is obtained by distilling a mixture of wood spirit with salicylic and sulphuric acids. This compound possesses the power of uniting with bases like an acid.

(1011) The following table shows the composition and some of the physical properties of the more important methylic ethers. The densities to which an asterisk is affixed were taken at 32° F.

Methyl = C_2H_3.	Formulæ.	Boiling point, °F.	Specific Gravity.	
			Liquid.	Vapour.
Oxide . . .	C_2H_3O, C_2H_3O			1·613
Sulphide . .	C_2H_3S, C_2H_3S	105·8	0·845	2·115
Bisulphide . .	$C_2H_3S_2, C_2H_3S_2$	about 240	1·048	3·310
Chloride . .	C_2H_3, Cl			1·731
Bromide . .	C_2H_3, Br	55·5	1·664*	
Iodide . . .	C_2H_3, I	111·4	2·1992*	4·883
Cyanide . .	C_2H_3, C_2N	170·6		1·45
Sulphate . .	$2\ C_2H_3O, S_2O_6$	370	1·324	4·565
Nitrate . . .	C_2H_3O, NO_5	151	1·182	2·640
Borate . . .	$3\ C_2H_3O, BO_3$	161·6	0·955	3·66
Formiate . .	$C_2H_3O, C_2\ H\ O_3$	92·1	0·9984*	2·084
Acetate . . .	$C_2H_3O, C_4\ H_3\ O_3$	133·3	0·9562*	2·563
Butyrate . .	$C_2H_3O, C_8\ H_7\ O_3$	204·6	0·9209*	3·52
Valerate . .	$C_2H_3O, C_{10}H_{11}O_3$	241·1	0·9015*	
Cyanate . .	$C_2H_3O, C_2\ N\ O$	about 104		
Cyanurate . .	$3\ C_2H_3O, C_6\ N_3\ O_3$	525		5·98
Benzoate . .	$C_2H_3O, C_{14}H_5\ O_3$	389·3		4·717
Oxalate . . .	$2\ C_2H_3O, C_4\ O_6$	321·8		
Salicylate . .	$C_2H_3O, C_{14}H_5\ O_5$	431·6	1·18	5·42

(1012) *Tritylic, Tetrylic, Amylic, and Octylic Ethers.*—1. *Tritylic Ether* was obtained by Chancel, but it is little known, and its derivatives have not yet been investigated. 2. *Tetrylic* (butylic) *Ether* was first described by Kolbe as one of the products of the voltaic decomposition of valerate of potash. Since that time, M. Wurtz has published a memoir on the ethers of the tetrylic series, to which the reader is referred for a description of their properties (*Ann. de Chimie,* III., xlii., 129). The amylic series has been more completely investigated, from the circumstance that the raw material (fousel oil) from which they are procured is an abundant secondary product which is separated from corn brandy and potato spirit during the process of rectification.

3. *Amylic Ether* ($C_{10}H_{11}O, C_{10}H_{11}O$) is obtained only in small quantity by the distillation of fousel oil with sulphuric acid, since by this method the greater part of the alcohol is converted into hydrocarbons isomeric with olefiant gas. Amylic ether boils at 349°. M. Balard states that he also procured it by decomposing chloride of amyl ($C_{10}H_{11}Cl$) by means of a concentrated solution of potash: the mixture is to be sealed up in a tube and heated for some time to 212°. The liquid which floats upon the surface has a fragrant odour, and

oils at about 233°. It is, however, doubtful, according to William-on, whether this is not the amylethylic ether. No analysis of t has been made. It is probable that some of the compound thers of the amylic series are the bodies to which the odour and avour of certain fruits belong, but they present no special points f interest, and therefore need no detailed description. They may be rocured by methods analogous to those which were described when reating of the different ethylic ethers. The amylic series was care-ully investigated by Cahours, (*Ann. de Chimie*, II., lxx. and lxxv.)

The following table contains the principal ethers of the tetrylic nd amylic groups:—

	Tetrylic (Butylic) Series.				Amylic Series.			
	Formulæ.	Boiling point, °F.	Sp. gr. Liquid.	Sp. gr. Vapour	Formulæ.	Boiling point. °F.	Sp. gr. Liquid.	Sp. gr. Vapour
Oxide . .					$C_{10}H_{11}O, C_{10}H_{11}O$	348·8		
Sulphide .					$C_{10}H_{11}S, C_{10}H_{11}S$	420·8		6·3
Bisulphide					$C_{10}H_{11}S_2, C_{10}H_{11}S_2$	480?	0·918	
Chloride .	C_8H_9Cl	160			$C_{10}H_{11}, Cl$	215		3·77
Bromide .	C_8H_9Br	192	1·274	4·72	$C_{10}H_{11}, Br$			
Iodide . .	C_8H_9I	249·8	1·604	6·217	$C_{10}H_{11}, I$	294·8	1·511	6·675
Cyanide .	C_8H_9, Cy	257	0·810	2·892	$C_{10}H_{11}, C_2N$	294·8	0·806	3·335
Nitrate .	C_8H_9O, NO_5	266			$C_{10}H_{11}O, NO_5$	298·4	0·994	
Acetate .	$C_8H_9O, C_4H_3O_3$	237	0·884	4·073	$C_{10}H_{11}O, C_4H_3O_3$	257		4·458
Carbonate.					$2C_{10}H_{11}O, C_2O_4$	435	0·914	
Oxalate .					$2C_{10}H_{11}O, C_4O_6$	503		8·4

4. Bouis has recently examined (*Ann. de Chimie*, III., xliv., 128) several of the ethers of the octylic (caprylic) series: many of them possess a very agreeable and fragrant odour, which may possibly lead to their employment as perfumes; but they do not present sufficient importance to require further notice in this work.

§ V. Action of Chlorine on the Ethers and Alcohols.

(1013) Chlorine exerts a powerful action upon the alcohols, and upon all their derivatives which contain hydrogen, forming by substitution numerous compounds, in which a certain number of equivalents of hydrogen are displaced by chlorine. Similar effects are produced by bromine and by iodine, though the action of these elements is less energetic. Solar light greatly increases the facility with which the reaction is effected. The general laws by which these substitutions are regulated will be best understood by the description of a few of the most important compounds thus formed.

(*a*) *Derivatives from Wine Alcohol.*

(1014) *Dichlorinated Ether* $2\,(C_4H_3Cl_2O)$. *Sp. gr.* 1·5008.—When dry chlorine is passed into anhydrous ether, abundance of hydrochloric acid is formed; 2 of the 5 equivalents of hydrogen in each half of the molecule of ether are displaced, and in their stead 2 equivalents of chlorine enter into the compound. 8 equivalents of chlorine, and 1 of ether, thus produce 4 equivalents of hydrochloric acid, and 1 of this new body:—

$$2\,\overbrace{\left(C_4\genfrac{}{}{0pt}{}{H_3}{H_2}O\right)}^{\text{Ether.}} + 8\,Cl = 4\,HCl + 2\,\overbrace{\left(C_4\genfrac{}{}{0pt}{}{H_3}{Cl_2}O.\right)}^{\text{Dichlorinated Ether.}}$$

It forms a heavy, colourless, oily liquid, neutral to litmus paper, with an odour and taste resembling that of fennel; at 284° it undergoes decomposition before it begins to boil, and by contact with water it is gradually converted into acetic and hydrochloric acids. It has been regarded by Liebig as a compound of the same order as acetic acid, and he terms it *oxychloride of acetyl*, $2\left(C_4\genfrac{}{}{0pt}{}{H_3}{Cl_2}O\right)$; 6 equivalents of water would produce, with 1 equivalent of this substance, 2 equivalents of dry acetic acid and 4 of hydrochloric acid; $2\left(C_4\genfrac{}{}{0pt}{}{H_3}{Cl_2}O\right) + 4\,HO = 2\,(HO, C_4H_3O_3) + 4\,HCl$. An alcoholic solution of potash immediately produces this decomposition, chloride of potassium and acetate of potash being formed.

Perchlorinated Ether (C_4Cl_5O, C_4Cl_5O). *Sp. gr. of solid* 1·9.—If ether, saturated with chlorine, be exposed in a vessel with excess of the gas, to the direct rays of the sun, a crystalline body is formed, which fuses at 156°. It is soluble in hot alcohol, and crystallizes on cooling in octohedra with a square base. This substance represents ether, in which the whole of the hydrogen has been displaced by chlorine. Under certain circumstances the perchlorinated ether, at the moment of its formation, is resolved into sesquichloride of carbon, and into a body corresponding to aldehyd, in which all the hydrogen has been displaced by chlorine: and a similar transformation occurs when the vapour of the chlorinated ether is exposed to a temperature of about 592°;

$$2\,\overbrace{(C_4Cl_5O)}^{\text{Perchlorin. Ether.}} \quad = \quad \overbrace{C_4Cl_6}^{\text{Sesquichlor. Carb.}} \quad + \quad \overbrace{C_4Cl_4O_2}^{\text{Perchloraldehyd.}}.$$

An alcoholic solution of potash decomposes perchlorinated ether, but the reaction is complicated, owing to the presence of compounds derived from the alcohol employed.

(1015) The action of chlorine upon chloride of ethyl is more regular; with suitable care it is possible to obtain compounds in which each equivalent of hydrogen is successively removed, and its place supplied by chlorine, as shown in the table given at page 46.

(1016) *Action of Chlorine upon Compound Ethers.*—The foregoing examples are true cases of substitution; but in some rare instances the chlorine unites directly with the compound, producing a new chlorinated body, without separation of hydrogen or formation of hydrochloric acid; an instance of this kind is presented in pyromucic ether (C_4H_5O, $C_{10}H_3O_5$), which absorbs 4 equivalents, or rather more than its own weight of chlorine, and from a crystalline solid becomes converted into a colourless syrupy liquid, C_4H_5O, $C_{10}H_3Cl_4O_5$. A more familiar example is offered in the direct union of chlorine and olefiant gas. These two gases, when mingled in equal measures, combine to form the oily liquid discovered by the Dutch chemists, and which, by the continued action of chlorine, yields a series of compounds, the last member of which is Faraday's sesquichloride of carbon (400).

The following table exhibits in one view the effect of chlorine in its successive stages upon ether, and some of its derivatives and compounds:—

	Normal Ethers.	Dichlorinated.	Perchlorinated.	Various stages.
Alcohol. . .	C_4H_5O,HO			$C_4HCl_3O_2$
Ether . . .	$2(C_4H_5O)$	$2(C_4H_3Cl_2O)$	$2(C_4Cl_5O)$	
Carbonic Ether	$2(C_4H_5O,CO_2)$	$2(C_4H_3Cl_2O,CO_2)$	$2(C_4Cl_5O,CO_2)$	
Oxalic Ether .	$2(C_4H_5O,C_2O_3)$		$2(C_4Cl_5O,C_2O_3)$	
Formic Ether .	C_4H_5O,C_2HO_3	$C_4H_3Cl_2O,C_2HO_3$	C_4Cl_5O,C_2ClO_3	
Acetic Ether .	$C_4H_5O,C_4H_3O_3$	$C_4H_3Cl_2O,C_4H_3O_3$	$C_4Cl_5O,C_4Cl_3O_3$	
Chloracetic do.	$C_4H_5O,C_4Cl_3O_3$		$C_4Cl_5O,C_4Cl_3O_3$	$C_4HCl_4O,C_4Cl_3O_3$
Benzoic do. .	$C_4H_5O,C_{14}H_5O_3$			$C_4H_3Cl_2,C_{14}H_5O_3$
Pyromucic do.	$C_4H_5O,C_{10}H_3O_5$			$C_4H_5O,C_{10}H_3Cl_4O_5$

Experiment shows that, whether ether be free or in combination, the first 2 equivalents of hydrogen are more readily removed from it than the others, as indeed might be expected from the facility with which alcohol loses 2 equivalents of hydrogen by oxidation in the manufacture of acetic acid. All the compounds indicated in the third column of the table are represented as containing $C_4H_2Cl_3O$; and when any one of these is submitted to the action of an alcoholic solution of hydrate of potash, it is decomposed; and acetate of potash, along with chloride of potassium, is found among the products. This circumstance can only be explained by supposing that, whenever the compound ethers of an organic acid into the composition of which hydrogen enters, are submitted to the action of chlorine, the hydrogen is in the first instance displaced from the ether, and subsequently, by prolonged continuance of the action, the displacement extends to the hydrogen co in the acid of the compound. The mode in which the nev undergo decomposition, in many instances affords proof t displacement is effected in this order. When, for example, rated formic ether is decomposed by an alcoholic solu potash, chloride of potassium, and acetate and formiate of t are the result :—

$$4\,KO + \overbrace{C_4H_3Cl_2O,\ C_2HO_3}^{\text{Dichloroformic Ether.}} = \overbrace{KO,\ C_4H_3O_3}^{\text{Acetate of Potash.}} + 2\,KCl + \overbrace{KO,\ (}^{\text{Formiate}}$$

Now the compound $C_4H_3Cl_2O$, when decomposed by potasl acetate of potash and chloride of potassium (1014), so t formiate is evidently derived from undecomposed formic a

When chlorine is made to act upon the ethers un conjoined influence of the sun's rays and of a high temp the whole of the hydrogen, both of the ether and of t combined with it, is displaced. These perchlorinated co ethers, such as the perchloracetic ether (C_4Cl_5O, $C_4Cl_3($ perchloroformic ether (C_4Cl_5O, C_2ClO_3), are very unstable. are readily decomposed by elevation of temperature, alcohol, as well as by solutions of ammonia, and of th alkalies. When the perchlorinated ethylic ethers are subject high temperature, the products obtained vary with the na the acid combined with the ether; but amongst these pr perchloraldehyd ($C_4Cl_4O_2$) is always present. This co is doubtless derived from the compound C_4Cl_5O, which al bodies contain, and which, at an elevated temperature yields sesquichloride of carbon C_4Cl_6 and perchloraldehyd (C When the decomposition is effected by alcohol, or by an al solution of potash, amongst other bodies trichloracetı (HO, $C_4Cl_3O_3$), or the products of its decomposition, is found. This substance is the result of the action of wat perchloraldehyd; hydrochloric acid being liberated, as is thus :—

$$\overbrace{C_4Cl_4O_2}^{\text{Perchloraldehyd.}} + 3\,HO = \overbrace{HO,\ C_4Cl_3O_3}^{\text{Chloracetic Acid.}} + HCl;$$

and when ammonia is made to act upon one of these perchlo ethers, trichloracetamide, which is always one of the prod obtained by the following reaction upon perchloraldehyd :—

$$\overbrace{C_4Cl_4O_2}^{\text{Perchloraldehyd.}} + \overbrace{H_3N}^{\text{Ammonia.}} = \overbrace{C_4Cl_3H_2NO_2}^{\text{Trichloracetamide.}} + KCl.$$

M. Cahours finds that the chloromethylic ethers are subject to similar general modes of decomposition, though of course the specific products differ from those yielded by the ethylic series.

It frequently happens, however, that the compound produced by the action of chlorine does not correspond in composition to the body which furnishes it; for in these cases the number of equivalents of hydrogen which is removed is greater than the number of equivalents of chlorine which enter into the compound. An example of this kind occurs when dry chlorine is transmitted through anhydrous alcohol, when the substance, described by Liebig under the name of *chloral*, is formed.

(1017) CHLORAL; *Trichloraldehyd* ($C_4Cl_3HO_2$). *Sp. gr. of liquid* 1·502; *of vapour* 5·13.—When pure anhydrous alcohol is submitted to the action of well-dried chlorine, it is decomposed; but 8 equivalents of chlorine are required for the decomposition of a single equivalent of alcohol; a copious disengagement of hydrochloric acid occurs, and chloral is formed. This body, however, does not correspond in composition to alcohol, but to aldehyd, 2 equivalents of hydrogen having been removed without any corresponding substitution of chlorine, whilst the other 3 equivalents of hydrogen have been displaced by chlorine in the usual manner. These relations will be at once perceived by comparing the formulæ;

Alcohol	$C_4H_6O_2$	or C_4H_5O, HO
Aldehyd	$C_4H_4O_2$	or C_4H_3O, HO
Chloral	$C_4Cl_3HO_2$	or C_4Cl_3O, HO;

and the reaction is represented by the equation:—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} + 8\,Cl = \overbrace{C_4Cl_3HO_2}^{\text{Chloral.}} + 5\,HCl.$$

If chlorine be passed into dilute instead of into anhydrous alcohol, no chloral is formed, but instead of it aldehyd, acetic acid, and hydrochloric acid are produced. In this case aldehyd appears to be the compound formed, and by a secondary reaction of aldehyd upon water at the moment of its formation, it appropriates 2 equivalents of oxygen from the water, whilst the chlorine removes the corresponding quantity of hydrogen:—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} + 2\,Cl = \overbrace{C_4H_4O_2}^{\text{Aldehyd.}} + 2\,HCl;\ \text{and}$$

$$\overbrace{C_4H_4O_2}^{\text{Aldehyd.}} + 2\,HO + 2\,Cl = \overbrace{C_4H_4O_4}^{\text{Acetic Acid.}} + 2\,HCl.$$

Chloral is, in many respects, a very remarkable body. In order to obtain it in a state of purity, the alcohol is subjected for many hours to a current of chlorine, which is transmitted so long as it is absorbed. It is necessary at first to keep the alcohol cool, but afterwards the temperature must be gradually raised until it boils. The crude product is mixed with three times its bulk of oil of vitriol, and distilled at a gentle heat. This operation is again repeated, and it is a third time distilled over quicklime. Stædeler finds that chloral may also be formed by distilling a mixture of one part of starch (or sugar) with 7 of hydrochloric acid and 3 of peroxide of manganese; formic and carbonic acids, and other bodies, accompany it.

Chloral is a colourless, oily-looking fluid, of a peculiar penetrating odour, which produces a flow of tears; when dropped upon paper it leaves a transient greasy stain. It boils at 201°, and is soluble in water, alcohol, and ether. If mixed with a small quantity of water, much heat is extricated, and a crystalline hydrate is formed in the same way as with the bichloride of tin. One of its most singular properties is the change which it undergoes spontaneously by keeping; in a few days it becomes converted into a tough white porcellanous-looking mass, isomeric with the liquid form, into which, by distillation, it can be again converted. This white substance is insoluble in alcohol, in ether, and in water, but by contact with water it is gradually converted into the crystallized hydrate of chloral. The facility of thus effecting its transformation into isomeric modifications indicates a certain resemblance to aldehyd in the instability of its molecular arrangement.

An alcoholic solution of potash converts chloral immediately into formiate of potash and chloroform,

$$\overbrace{C_4Cl,\ HO_2}^{\text{Chloral.}} + KO,\ HO = \overbrace{KO,\ C_2HO_3}^{\text{Formiate of Potash.}} + \overbrace{C_2HCl_3}^{\text{Chloroform.}}.$$

This fact cannot, however, be supposed to indicate much respecting the grouping of the component molecules of chloral, the unstable equilibrium of which is evidenced by the facility with which chloral spontaneously passes from the liquid to the solid form. There is no doubt that the arrangement is very different in these two forms, and if thus, whilst unsolicited by any extraneous chemical forces, its molecular arrangement is so readily altered, it is obvious that the results of decomposition, under the influence of powerful chemical agents, will throw but little light upon the probable arrangement of its constituent elements.

(1018) ***Perchloraldehyd*** ($C_4Cl_4O_2$). *Sp. gr. of liquid* 1·603; *of vapour* 6·32—This body is obtained by transmitting the vapour of perchlorinated ether 2 (C_4Cl_5O) through heated tubes (1014), a mixture of sesquichloride of carbon and perchloraldehyd being the result:—

$$2\,(\overbrace{C_4Cl_5O}^{\text{Perchlor. Ether.}}) = \overbrace{C_4Cl_6}^{\text{Sesquichlor. Carbon.}} + \overbrace{C_4Cl_4O_2}^{\text{Perchloraldehyd.}}.$$

The two compounds may be separated by distillation, since the chloride of carbon is the less volatile of the two. Perchloraldehyd is also always one of the products of the decomposition of the compound chlorinated ethylic ethers by heat (1016), of which the following may be taken as examples:—

$$\overbrace{C_4Cl_5O,\ C_2ClO_3}^{\text{Perchloroformic Ether.}} = \overbrace{C_4Cl_4O_2}^{\text{Perchloraldehyd.}} + \overbrace{C_2O_2Cl_2}^{\text{Phosgene.}}.$$

$$\overbrace{C_4Cl_5O,\ C_4Cl_3O_3}^{\text{Perchloracetic Ether.}} = \overbrace{2\,(C_4Cl_4O_2)}^{\text{Perchloraldehyd.}}.$$

$$\overbrace{2\ C_4Cl_5O,\ C_4O_6}^{\text{Perchloroxalic Ether.}} = \overbrace{2\,(C_4Cl_4O_2)}^{\text{Perchloraldehyd.}} + \overbrace{C_2O_2Cl_2}^{\text{Phosgene.}} + 2\ Cl.$$

It is a transparent, fuming, volatile liquid, which emits a suffocating odour, and boils at 244°. It turns the skin white if allowed to fall upon it. Water decomposes it gradually into hydrochloric and trichloracetic acids:—

$$\overbrace{C_4Cl_4O_2}^{\text{Perchloraldehyd.}} + 3\,HO = \overbrace{HO,\ C_4Cl_3O_3}^{\text{Trichloracetic Acid.}} + HCl.$$

Bromine acts upon alcohol in a manner similar to chlorine, forming *bromal* ($C_4Br_3HO_2$), which is a colourless oil of sp. gr. 3·34, boiling above 212°.

(*b*) *Chlorinated Derivatives from other Alcohols and their Ethers.*

It will be unnecessary to enter into any detailed description of the innumerable compounds which may be formed from the simple and compound ethers of the other alcohols, by the substitution of chlorine, bromine, and iodine for hydrogen; for, with one exception, which occurs in the case of chloroform, they present but little to arrest the attention of the chemist. They have been minutely studied by Malaguti, Cahours, and Cloez, to whose various papers in the *Annales de Chimie*, the reader is referred for further information on the subject.

(1019) CHLOROFORM (C_2HCl_3), *Sp. gr. of liquid* 1·497; *of vapour* [illegible]—This interesting compound is produced by a variety of reactions; when chlorine is made to act upon chloride of methyl, the following change occurs:—

$$\overbrace{C_2H_3Cl}^{\text{Chloride of Methyl.}} + 4Cl = \overbrace{C_2HCl_3}^{\text{Chloroform.}} + 2\,HCl.$$

Another remarkable mode of its formation has been pointed out by Dumas, who finds that a mixture of equal volumes of marsh gas and [illegible], to which an excess of chlorine is added, [illegible] an oily liquid consisting of chloroform and bichloride of carbon. It is also produced during the decomposition of the trichloracetates by the hydrated alkalies:—

$$\overbrace{KO, C_4Cl_3O_3}^{\text{Trichloracetate Potash.}} + KO, HO = \overbrace{2\,KO, CO_2}^{\text{Carb. Potash.}} + \overbrace{C_2HCl_3}^{\text{Chloroform.}}.$$

And lastly by the action of the hydrated alkalies upon chloral:

$$\overbrace{C_4HCl_3O_2}^{\text{Chloral.}} + KO, HO = \overbrace{C_2HCl_3}^{\text{Chloroform.}} + \overbrace{KO, C_2HO_3}^{\text{Formiate Potash.}}$$

But it is most economically obtained by acting upon dilute alcohol with chloride of lime (bleaching powder). Wood spirit, acetone, oil of turpentine, and many essential oils yield it likewise under the influence of chloride of lime. Chloroform is readily procured in a state of purity by the following process: 6 parts of chloride of lime, 24 parts of water, and 1 part of alcohol are to be mixed in a capacious still, and the temperature raised as rapidly as possible till it reaches 180°. The distillation is then continued until about one part and a half have passed over; the products, consisting chiefly of chloroform accompanied by water, collect in two layers in the receiver—the chloroform constituting the lower layer. It should be decanted from the aqueous portion and agitated with oil of vitriol in order to destroy traces of volatile oils which accompany it; by another rectification it is obtained in a state of purity.

Chloroform is a colourless, volatile liquid, of high refracting power, the boiling point of which is 142° F. It has a powerful agreeable ethereal odour, and a sweet penetrating taste. Alcohol and ether dissolve it in every proportion, but it is very sparingly soluble in water. Concentrated sulphuric acid has no action upon it, and even potassium does not occasion its decomposition. It is inflamed with difficulty, and burns with a green flame. By mixing it with an alcoholic solution of potash it is decomposed; chloride of potassium, and formiate of potash being produced:—

$$\overbrace{C_2HCl_3}^{\text{Chloroform.}} + 4\,(KO, HO) = 3\,KCl + \overbrace{KO, C_2HO_3}^{\text{Formiate of Potash.}} + 4\,HO.$$

Aqueous solution of potash does not produce this change, owing to the sparing solubility of chloroform in water.

The vapour of chloroform possesses the remarkable power of producing, in the person who has respired it, complete temporary insensibility to pain. It may be readily inhaled for this purpose by placing a small quantity of the liquid upon a sponge or a handkerchief which is to be held before the mouth and nostrils. Professor Simpson, of Edinburgh, has the merit of having been the first to apply this property to the alleviation of human suffering; and since the period when he showed its efficacy for this purpose, it has been extensively employed for rendering patients insensible to pain during severe surgical operations.

It is of great importance that the chloroform used for this purpose should be quite pure. In some cases it has been found when exposed to a strong light to have undergone spontaneous decomposition. It ought to communicate no colour to oil of vitriol when agitated with it. The liquid itself should be free from colour, and it should be perfectly destitute of any chlorous odour. When a few drops are allowed to evaporate on the hand no unpleasant odour should be left.

Chloroform has been regarded as anhydrous formic acid, in which the three equivalents of oxygen are displaced by chlorine: but the mode in which it is obtained by substitution from chloride of methyl shows that this cannot be its true constitution; it probably ought to be regarded as the homologue of methylic ether in which two of the equivalents of hydrogen are displaced by chlorine, C_2H_3Cl, becoming $C_2\left.\begin{matrix}H\\Cl_2\end{matrix}\right\}Cl$. If distilled in a current of dry chlorine, chloroform is wholly deprived of hydrogen, and yields bichloride of carbon (326), and hydrochloric acid; $C_2\left.\begin{matrix}H\\Cl_2\end{matrix}\right\}Cl + 2\,Cl = C_2Cl_4 + HCl$.

Chloroform freely dissolves sulphur, phosphorus, and iodine. It is also a good solvent for fatty and resinous bodies. No other liquid is so perfect a solvent for caoutchouc, which is left unaltered by it on evaporation. Lower chlorides derived from wood spirit having the formulæ (C_2HCl_2) and (C_2HCl) have also been obtained.

Iodoform (C_2HI_3), is a solid, of a yellow colour, in which 3 equivalents of iodine occupy the place of the chlorine in chloroform. A corresponding compound with bromine may likewise be formed.

§ VI. ON THE HYDROCARBONS DERIVABLE FROM THE ALCOHOLS.

(1020) Allusion has already been made to a series of hydrocarbons homologous with olefiant gas, which are derivable from the alcohols, and the process of preparing olefiant gas itself has been described (399). But besides the homologues of olefiant gas, two additional series of hydrocarbons may be obtained from the alcohols; for the knowledge of these compounds we are indebted to the researches of Kolbe and Frankland. One series of these bodies corresponds to the radicle of the alcohol 2 (C_nH_{n+1}), the other to the hydride of that radicle (C_nH_{n+1},H). The table on the following page contains the more important members of each of these groups at present known.

(*a*) *Hydrocarbons homologous with Olefiant Gas* (C_nH_n).

(1021) The compounds belonging to this series are generally formed by the action of sulphuric acid or of chloride of zinc upon their corresponding alcohols, from which they differ by containing the elements of two equivalents less of water; for instance,—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} \quad - \quad 2\,HO \quad = \quad \overbrace{C_4H_4}^{\text{Olefiant Gas.}}\text{; and}$$

$$\overbrace{C_{10}H_{12}O_2}^{\text{Fousel Oil.}} \quad - \quad 2\,HO \quad = \quad \overbrace{C_{10}H_{10}}^{\text{Amylene.}}.$$

They may also be obtained by the decomposition of the hydrochloric ether of the particular alcohol by exposing it to an elevated temperature; under these circumstances the ether is resolved into hydrochloric acid, and the hydrocarbon of the alcohol, thus;—

$$\overbrace{C_2H_3Cl}^{\text{Chloride of Methyl.}} \text{ yields } \overbrace{C_2H_2}^{\text{Methylene.}} \quad + \quad HCl\text{; and}$$

$$\overbrace{C_4H_5Cl}^{\text{Chloride of Ethyl.}}\text{, becomes } \overbrace{C_4H_4}^{\text{Olefiant Gas.}} \quad + \quad HCl.$$

The formation of these compounds however does not appear to consist simply in the abstraction of water from the alcohol; for, in some cases, the substance which is obtained has a vapour density double of that which the corresponding hydrocarbon should possess: when, for instance, fousel oil is distilled with sulphuric acid, the hydrocarbon which is liberated is not amylene ($C_{10}H_{10}$), for it has

1. Olefiant Gas Series (C_nH_n).					2. Alcohol Radicles ($C_nH^{n+}{}_1$, C_nH_{n+1})					3. Hydrides of the Alcohol Radicles (C_nH_{n+2})				
	Formula	Boiling Point, ° F.	Specific Gravity.			Formula.	Boiling Point, ° F.	Specific Gravity.			Formula.	Boiling Point.	Specific Gravity.	
			Liquid.	Vapour.				Liquid.	Vapour.				Lid .	Vapour.
Methylene .	C_2H_2			0·490	Methyl .	C_2H_3, C_2H_3			1·036	Marsh gas, (Hydride of methyl)	C_2H_3, H		0·557	
Olefiant gas (Ethylene)	C_4H_4			0·978	Ethyl. .	C_4H_5, C_4H_5	—9·4		2·046	Hydride of ethyl . .	C_4H_5, H		1·075	
Tritylene (Propylene)	C_6H_6			1·498										
Oil gas, (Tetrylene, Butylene)	C_8H_8	0		1·852	Tetryl (Butyl)	C_8H_9, C_8H_9	222·8	0·705	4·070	Hydride of tetryl . .	C_8H_9, H			
Amylene . .	$C_{10}H_{10}$	102		2·386	Amyl . .	$C_{10}H_{11}$ $C_{10}H_{11}$	311·0	0·741	4·899	Hydride of amyl . .	$C_{10}H_{11}$, H	86	0·638	2·5
Hexylene (Caproylene)	$C_{12}H_{12}$	131		2·875	Hexyl	$C_{12}H_{13}$ $C_{12}H_{13}$	395·6	0·757	5·983					
Heptylene (Œnanthylene) . .	$C_{14}H_{14}$	122°?												
Octylene (Caprylene)	$C_{16}H_{16}$	257	0·723	3·90	Octyl (Capryl)	$C_{16}H_{17}$, $C_{16}H_{17}$								
Nonylene (Elaene) .	$C_{18}H_{18}$	230		4·48										
Paramylene .	$C_{20}H_{20}$	320		5·061										
Cetylene . .	$C_{32}H_{32}$	527		8·007										

undergone condensation, and has been converted into the polymeric paramylene ($C_{20}H_{20}$), the vapour of which has a density exactly double of that of the true amylene obtained by distilling fousel oil with chloride of zinc.

Considerable difference of opinion exists as to the rational constitution of these hydrocarbons, which are regarded by Liebig as hydrides of the radicles of the fatty acids; thus he represents olefiant gas as consisting of (C_4H_3, H), or as *hydride of acetyl.*

The hydrocarbons of this class combine readily with anhydrous sulphuric acid, and with perchloride of antimony: they are also slowly absorbed by oil of vitriol when briskly agitated with it, and the solution when diluted with water and distilled, yields the corresponding alcohol. These hydrocarbons also combine with two equivalents of chlorine, bromine, and iodine, forming compounds which correspond with Dutch liquid in composition, and from which a similar series of substitution products may be obtained: for example,

Ethylic Dutch liquid $C_4H_4Cl_2$, or C_4H_3Cl, HCl.
Tritylic do. do. $C_6H_6Cl_2$, or C_6H_5Cl, HCl.
Amylic do. do. $C_{10}H_{10}Cl_2$, or $C_{10}H_{11}Cl, HCl$.

The following are the more important of these hydrocarbons:—

1. *Methylene* (C_2H_2). Dumas and Péligot obtained this gaseous body by transmitting the gaseous chloride of methyl through a red-hot porcelain tube; C_2H_3Cl becoming $C_2H_2 + HCl$.

2. *Ethylene, Olefiant Gas,* or *Ethyl* (C_4H_4) has already been described (399). It is produced abundantly during the dry distillation of pit coal, and of many fatty and resinous bodies. It is the principal luminous constituent of coal gas. When required in a state of purity it is always obtained by decomposing alcohol by means of sulphuric acid in excess.

3. *Tritylene, Propylene* (C_6H_6), *Sp. gr.* 1·498. Reynolds obtained this gas mixed with marsh gas and some other compounds, by decomposing the vapours of fousel oil by transmission through a porcelain tube heated to redness; but it is best procured by the action of iodide of phosphorus (PI_2) upon glycerin (*note,* 1147).

4. *Tetrylene, Butylene,* or *Oil Gas* (C_8H_8), has been already described (405). This gas was ascertained by Faraday to be one of the products furnished by the destructive distillation of oil; and it appears also to be contained amongst the products of the distillation of caoutchouc. It was afterwards obtained by Kolbe during the voltaic decomposition of valerate of potash; and by Wurtz as

one of the compounds produced by the action of chloride of zinc upon tetrylic alcohol.

5. *Amylene* ($C_{10}H_{10}$) may be procured by decomposing chloride of amyl by fused hydrate of potash, or by distilling a concentrated solution of chloride of zinc with fousel oil; or by acting upon iodide of zinc in a sealed tube with an amalgam of zinc: in the latter case it is mixed with hydride of amyl. Amylene is a colourless, very mobile liquid, with the odour of decaying cabbage. It boils at 102°.

6. *Hexylene; Caproylene* ($C_{12}H_{12}$). This compound is a colourless liquid lighter than water, of a nauseous, penetrating, alliaceous odour. It is scarcely soluble in water, but freely so in alcohol and ether. It appears to act injuriously when respired; the boiling point is 131°. It is obtained during the destructive distillation of several fatty acids (Fremy).

7. *Heptylene* or *Œnanthylene* ($C_{14}H_{14}$) was obtained by Bouis from the distillation of œnanthol (977) with anhydrous phosphoric acid. It is a liquid which boils at about 122°.

8. *Octylene; Caprylene* ($C_{16}H_{16}$) was obtained as a colourless liquid, insoluble in water, and boiling at 257°, by distilling the castor oil (octylic) alcohol with sulphuric acid, or chloride of zinc. The action of potassium or of mercury on chloride or iodide of octyl gives rise to the same compound;

$$C_{16}H_{17}I + Hg_2 = C_{16}H_{16} + Hg_2I + H.$$

9. *Nonylene,* or *Elaene* ($C_{18}H_{18}$) was obtained mixed with hexylene by Fremy, during the distillation of several fatty acids.

10. *Paramylene* ($C_{20}H_{20}$) is procured by the distillation of fousel oil with anhydrous phosphoric acid in excess. Its boiling point is as high as 320°, that of amylene being only 102°. Fousel oil, it will be seen, gives rise to three isomeric hydrocarbons of this series, viz., to tritylene, amylene, and paramylene.

(*b*) *On the Hydrocarbon Radicles of the Alcohols* $2\,(C_nH_{n+1})$.

(1022) The first substance of this class which was obtained in an isolated form, was the radicle of tetrylic alcohol, which was procured by Kolbe during the electrolysis of valerate of potash, and was by him termed valyl, $2\,(C_8H_9)$; other hydrocarbons homologous with tetryl, have been obtained by the electrolytic decomposition of the salts of the volatile fatty acids (871) (1153); and subsequently a general method of obtaining these bodies was contrived by Frankland, who decomposes the hydriodic ether of the alcohol by means of zinc, at a high temperature in sealed tubes. Mr. G. Williams has recently succeeded in isolating tetryl, $2\ C_8H_9$, from the products of the destructive distillation of coal at low temperatures, and he considers it highly probable that several other radicles of this class may be found amongst the numerous hydrocarbons which are formed during the distillation of this mineral.

The hydrocarbons of this class have not hitherto been made to combine directly with chlorine, bromine, or iodine, so as to reproduce the corresponding hydrochloric, hydrobromic, or hydriodic ether; for when exposed to the influence of the halogens, various substitution compounds are produced. Some chemists, including Hofmann and Gerhardt, when Frankland first announced the isolation of these compounds, considered this as a strong argument against the admission of the view that they were truly alcohol radicles, and they proposed to view them as homologues of marsh gas: but the subsequent isolation of the true homologues of marsh gas which constitute the hydrides of the alcohol radicles (1025), has weakened the force of this objection. The bodies which we have termed alcohol radicles, may very consistently be regarded as analogues of hydrogen gas, which many chemists suppose, when in its free state, not to be a simple body, but a compound of hydrogen with itself, in short, a hydride of hydrogen $\left.\begin{matrix}H\\H\end{matrix}\right\}$ and the radicle of alcohol may in like manner be considered as ethylide of ethyl, $\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}$, a view which is now very generally adopted, and the correctness of which, the discovery of the double radicles of Wurtz (to which we shall presently refer) may almost be said to have proved. The alcohol radicles are not absorbed by anhydrous sulphuric acid, or by oil of vitriol, but are completely soluble in alcohol.

These hydrocarbons appear to belong to the hydrogen or metallic type $\left.\begin{matrix}H\\H\end{matrix}\right\}$, and are represented by the formula $\left.\begin{matrix}C_nH_{n+1}\\C_nH_{n+1,}\end{matrix}\right\}$ an equivalent of the compound $2\ (C_nH_{n+1})$, yielding 4 volumes of vapour. They would therefore stand to the third series of hydrocarbons (C_nH_{n+2}), which are next to be described, in a relation similar to that of ether to alcohol, thus:—

$$\begin{array}{cc}
\text{Ether.} & \text{Ethyl.} \\
\overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2} & \overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}} \\
\text{Alcohol.} & \text{Hydride of Ethyl.} \\
\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2} & \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}
\end{array}$$

M. Wurtz (*Ann. de Chimie*, III. xliv. 275), following up the ideas of Williamson and Brodie upon the double ethers, has succeeded in obtaining compounds in which the second equivalent of the hydrocarbon is displaced by the hydrocarbon of a different alcohol, thus forming a series of double radicles corresponding with Williamson's double ethers. If a mixture of the hydriodic ethers of the two alcohols in equivalent proportions be decomposed by means of sodium, the two radicles combine at the moment of their liberation, and form a new double radicle. Thus, in the preparation of ethyl-amyl, the following reaction occurs:—

$$\overbrace{C_4H_5I}^{\text{Iodide of Ethyl.}} + \overbrace{C_{10}H_{11}I}^{\text{Iodide of Amyl.}} + 2\,Na = 2\,NaI + \overbrace{C_4H_5,\,C_{10}H_{11}}^{\text{Ethyl Amyl.}}.$$

The discovery of these compounds confirms in a striking manner the ingenious hypothesis of Brodie (*Q. J. Chem. Soc.*, iii. 411), as to the mode in which these alcohol radicles are produced.

When zinc is made to decompose anhydrous iodide of ethyl, the first effect does not consist in the liberation of ethyl, but in the formation of a new compound, zinc-ethyl. This stage is rendered more evident by mixing the iodide of ethyl with its own bulk of ether, in which liquid the products of the reaction are soluble. Thus;—

$$\overbrace{C_4H_5I}^{\text{Iodide of Ethyl.}} + Zn\,Zn = \overbrace{C_4H_5Zn}^{\text{Zinc Ethyl.}} + ZnI.$$

This zinc-ethyl then reacts upon a fresh portion of iodide of ethyl, and thus the ethyl is produced by an ordinary double decomposition; the molecule of ethyl from zinc-ethyl, combining at the moment of its liberation with the molecule of ethyl from the iodide of ethyl, as thus represented:—

$$\overbrace{C_4H_5I}^{\text{Iodide of Ethyl.}} + \overbrace{C_4H_5Zn}^{\text{Zinc Ethyl.}} = ZnI + \overbrace{C_4H_5,\,C_4H_5}^{\text{Ethyl.}}.$$

If water be present, the result is the formation of a hydrocarbon of a different kind, which may be regarded as ethyl, in which one of the molecules of ethyl is displaced by hydrogen.* In that case the decomposition would be:—

$$HO + \overbrace{C_4H_5I}^{\text{Iodide of Ethyl.}} + Zn\,Zn = \overbrace{C_4H_5,\,H}^{\text{Hydride of Ethyl.}} + ZnI + ZnO;$$

and Wurtz's double radicles would be merely compounds, in which

---

*** At present no compound of zinc with hydrogen (HZn) corresponding to zinc-ethyl is known, though there is nothing improbable in the existence of such a body.**

the place of the molecule of hydrogen, or of the ethyl, by a different hydrocarbon :—

Hydride of ethyl	C_4H_5, H.
Ethyl (ethylide of ethyl) . .	C_4H_5, C_4H
Ethyl-amyl (ethylide of amyl) .	C_4H_5, C_{10}I

It is interesting to remark, that the boiling po double radicles rises gradually as the number of e carbon and hydrogen increases, and that this regular p observed in the simple alcohol radicles when compare as in the following table; the boiling point and vapo the simple alcohol radicles being such as would the assigned to them upon the view above given; showi the simple and the double radicles are formed upo molecular plan :—

Double Radicles.	Formulæ. (Each yielding four volumes of vapour.)	Boiling point ° F.	Speci	
			Vapou	
			Expt.	T
Ethyl (Ethylide of ethyl) . .	$C_8H_{10} = C_4H_5, C_4H_5$	—9·4	2·046	2
Ethyl-tetryl . .	$C_{12}H_{14} = C_4H_5, C_8H_9$	143·6	3·053	2
Ethyl-amyl . .	$C_{14}H_{16} = C_4H_5, C_{10}H_{11}$	190·4	3·522	3
Methyl-hexyl . .	$C_{14}H_{16} = C_2H_3, C_{12}H_{13}$	179·6?	3·426	3
Tetryl (Tetrylide of tetryl) . .	$C_{16}H_{18} = C_8H_9, C_8H_9$	222·8	4·070	3
Tetryl-amyl . .	$C_{18}H_{20} = C_8H_9, C_{10}H_{11}$	269·6	4·465	4
Amyl (Amylide of amyl) . .	$C_{20}H_{22} = C_{10}H_{11}, C_{10}H_{11}$	311	4·899	4
Tetryl-hexyl . .	$C_{20}H_{22} = C_8H_9, C_{12}H_{13}$	311	4·917	4
Hexyl (Hexylide of hexyl) . .	$C_{24}H_{26} = C_{12}H_{13}, C_{12}H_{13}$	395·?	5·983	5

It may further be remarked, in illustration of the of the original molecular arrangement of the componer these compound bodies, that Wurtz finds that amyl p rotatory action on a ray of polarized light when it these compounds, ethyl-amyl displaying the power of polarized ray to the right; whilst amylene, valeric acid derivatives of amylic alcohol, in which there is reason that the molecule of amyl is destroyed, exert no rotator

(1023) 1. *Ethyl* (C_4H_5, C_4H_5); *Sp. gr. of gas* 2·046. mixture of granulated zinc and iodide of ethyl is sealed up glass tube from which air has been exhausted, and expo hours in an oil bath to a temperature of 300°, the iodi is gradually decomposed; the sides of the tube become c a white crystalline substance, and a colourless mobile liquid, equal in bulk to about half that of the iodide of ethyl employed, is formed. This liquid is a mixture of ethyl, with other hydrocarbons (olefiant gas, and hydride of ethyl, the product of a secondary decomposition), the hydrocarbons having been liquefied by the pressure of their own vapour, whilst the crystals consist of a compound of zinc-ethyl (C_4H_5, Zn) with iodide of zinc. On breaking off the capillary extremity of the tube under water, the whole of the liquid portion rapidly disappears, and escapes in the gaseous form. By collecting the portions which pass off last, the ethyl, which is the least volatile of these gases, is obtained nearly in a state of purity (Frankland, *Quart. Journ. Chem. Soc.* ii. 281).

Ethyl is a colourless gas with a slight ethereal smell; it burns with a highly luminous flame. At a temperature of 0° it remains gaseous under the ordinary atmospheric pressure, but it becomes liquefied at 38°, under a pressure of 2½ atmospheres. Frankland estimates its boiling point at about $-9°$, when the barometer stands at 30 inches. Ethyl is insoluble in water, but freely soluble in alcohol, which dissolves about 18 times its bulk of the gas, and gives it off when diluted with water. Chlorine has no action upon ethyl in the dark, but in diffused light it immediately combines with it and forms a colourless liquid.

2. *Methyl* (C_2H_3, C_2H_3), *Sp. gr.* 1·0365, is a gaseous body which burns with a bluish feebly luminous flame; it is not liquefied by a cold of 0° F. Methyl is obtained by acting upon iodide of methyl with zinc, exactly in the manner directed for the preparation of ethyl. When mixed with twice its bulk of chlorine in the dark, and afterwards brought into diffused daylight, no change of volume takes place, but a mixture of 2 volumes of hydrochloric acid, and 1 volume of a chlorinated compound, C_2H_2Cl, is formed.

3. *Tetryl, Butyl,* or *Valyl* (C_8H_9, C_8H_9); *Sp. gr. of liquid* 0·7057 at 32°; *of vapour* 4·070.—This compound is one of the products obtained during the electrolysis of the valerate of potash. It may also be prepared by the action of sodium upon iodide of tetryl, in a flask connected with a vertical condenser, so arranged that the volatilized products shall return constantly into the flask as fast as they are volatilized and condensed. When the reaction has terminated, the tetryl may be distilled off by a temperature not exceeding 300°. Tetryl boils at 222°·8.

4. *Amyl* ($C_{10}H_{11}$, $C_{10}H_{11}$); *Sp. gr. at* 32°, 0·7413; *of vapour* 4·899. —Frankland obtained this hydrocarbon by heating iodide of amyl with an amalgam of zinc in sealed tubes for some hours to a tem-

perature of from 320° to 360°. It may also be procured by the electrolysis of caproate of potash, or still more easily as advised by Wurtz, by the action of sodium on iodide of amyl. It is a colourless liquid, which boils at 311°, and has a somewhat aromatic odour. It exerts a right-handed rotatory action on a ray of polarized light, the degree of which appears to vary in different specimens, being connected with the power exerted by that of the fousel oil from which the radicle was prepared, some samples of fousel oil having a greater rotatory power than others.

5. *Hexyl, or caproyl* ($C_{12}H_{13}$, $C_{12}H_{13}$) was obtained by the voltaic decomposition of œnanthylate of potash. It is a liquid of an agreeable aromatic odour; its boiling point is about 395°.

(1024) Double Hydrocarbon Radicles.—*Ethyl-tetryl* (C_4H_5, C_8H_9), *Sp. gr. of liquid at* 32°, 0·7011; *of vapour* 3·053.—This compound was obtained by decomposing a mixture of 40 parts of iodide of tetryl, and 34 of iodide of ethyl, with 11 of sodium, in the manner already described for procuring tetryl: by distillation of the product, collecting that which passes over between 140° and 155°, and again rectifying it, a mobile liquid is obtained, the boiling point of which when pure is fixed at 143°·6. By a similar method, employing mixtures of the corresponding hydriodic ethers, M. Wurtz succeeded in obtaining other analogous compounds, which are enumerated in the table, page 194.

(*c*) *Hydrocarbons homologous with Marsh Gas* (C_nH_{n+2}).

(1025) When the hydriodic ethers are submitted to the action of zinc at a high temperature, other hydrocarbons are formed in addition to the radicles already described; the alcohol radicle itself undergoing a secondary decomposition into two hydrocarbons, which are complementary to each other. Ethyl, for example, breaks up into olefiant gas and hydride of ethyl; and amyl, in like manner, yields hydride of amyl, and a corresponding hydrocarbon:—

$$\overbrace{C_4H_5, C_4H_5}^{\text{Ethyl.}} \text{ becoming } \overbrace{C_4H_5, H}^{\text{Hydride of Ethyl.}} + \overbrace{C_4H_4}^{\text{Olefiant Gas.}}; \text{ and}$$

$$\overbrace{C_{10}H_{11}, C_{10}H_{11}}^{\text{Amyl.}} \text{ becoming } \overbrace{C_{10}H_{11}.H}^{\text{Hydride of Amyl.}} + \overbrace{C_{10}H_{10}}^{\text{Amylene.}}.$$

The hydrocarbons of this class are not absorbed by anhydrous sulphuric acid or by oil of vitriol, and are not acted upon by chlorine or by iodine in the dark, but in diffused daylight chlorine slowly gives rise to substitution compounds. Perchloride of antimony is without action upon them.

These hydrocarbons may also be formed by the regulated action of water upon the metallic compounds of zinc with the alcohol radicles. Thus :—

$$\overbrace{C_2H_3, Zn}^{\text{Zinc Methyl.}} + HO = \overbrace{C_2H_3, H}^{\text{Marsh Gas, or Hydride of Methyl.}} + ZnO$$

$$\overbrace{C_4H_5, Zn}^{\text{Zinc Ethyl.}} + HO = \overbrace{C_4H_5, H}^{\text{Hydride of Ethyl.}} + ZnO$$

$$\overbrace{C_{10}H_{11}, Zn}^{\text{Zinc Amyl.}} + HO = \overbrace{C_{10}H_{11}, H}^{\text{Hydride of Amyl.}} + ZnO$$

Each of the hydrocarbons of this group, with the exception of marsh gas, is isomeric with one of the group of alcohol radicles, although not identical with it; for example :—

			C_2H_4		C_2H_3, H*	Marsh Gas
Methyl . . .	C_2H_3, C_2H_3*	=	C_4H_6	=	C_4H_5, H*	Hydride of Ethyl
Methyl-ethyl .	C_2H_3, C_4H_5	=	C_6H_8	=	C_6H_7, H	Hydride of Trityl
Ethyl . . .	C_4H_5, C_4H_5*	=	C_8H_{10}	=	C_8H_9, H*	Hydride of Tetryl
Methyl-tetryl	C_2H_3, C_8H_9	=	$C_{10}H_{12}$	=	$C_{10}H_{11}, H$*	Hydride of Amyl

Those compounds marked with an asterisk have been already prepared, and the others might be easily procured, if needed.

(1026) 1. *Hydride of Methyl; Sp. gr.* 0·5596.—This compound has already been described under the name of *marsh gas* (401).

2. *Hydride of Ethyl* (C_4H_5, H); *Sp. gr.* 1·075.—This compound is a permanent gas, destitute of smell or taste. It is insoluble in water, but alcohol takes up more than its own bulk of it. The best manner of preparing it consists in decomposing a mixture of equal parts of water and iodide of ethyl, by means of zinc, in a sealed tube, at a temperature of about 330°, as already described when speaking of ethyl (1023). After the lapse of a couple of hours, the tube is opened under water, and the gas escapes with great violence. It may also be obtained by decomposing hydrocyanic ether with potassium. The potassium is placed in a flask, fitted with a condenser, and a bent tube for carrying off the gas as it is disengaged; the ether is allowed to fall, drop by drop, upon the potassium, whilst the gas which is disengaged is collected over water. Cyanide of potassium and cyanethine (997) remain in the retort, and hydride of ethyl is obtained in the gaseous state.

3. *Hydride of tetryl* (C_8H_9, H) is one of the products of the decomposition of tetrylic alcohol when distilled with chloride of zinc. It is liquefiable at a few degrees below 32°.

4. *Hydride of Amyl* ($C_{10}H_{11}$,H); *Sp.gr.of liquid* 0·638; *of vapour* 2·5.—This body was obtained by Frankland by acting on equal bulks of iodide of amyl and water, by means of zinc in a sealed tube, at

a temperature not exceeding 300°. Frankland considers it probable that it is identical with *Eupione*, which Reichenbach obtained during the rectification of the products from wood-tar; and he also thinks that it constitutes one of the condensible hydrocarbons of coal gas, a view which has been strengthened by the subsequent experiments of Greville Williams.

Hydride of amyl is a volatile, mobile, colourless liquid, with an odour resembling that of chloroform. It has a smaller density than any other known liquid; it remains unfrozen at —11°, and boils at 86°. Its vapour burns with a brilliant white flame, without smoke.

§ VII. ORGANIC BASES DERIVED FROM THE ALCOHOLS.

(1027) *Bases obtained by Substitution from Ammonia.*—Allusion has been already made (1022) to the remarkable manner in which the hydrogen in ammonia may be displaced by the hydrocarbons which are supposed to form the radicles of the alcohols; and in consequence of this kind of substitution, compounds are produced in which the basic character of the ammonia is fully preserved, and a new series of highly interesting bodies is obtained. The first bases of this description were procured by Wurtz, who found that when the cyanic ether, or its polymeride, the cyanuric ether of any of the alcohols, or the corresponding urea (1007), was distilled with hydrate of potash, a volatile base was obtained homologous with ammonia, but containing the radicle of the alcohol corresponding to the compound subjected to distillation; for example,

$$\overbrace{C_2H_3O,\ C_2NO}^{\text{Methyl-cyanic Ether.}} + 2(KO,\ HO) = \overbrace{\left.\begin{matrix}C_2H_3\\H_2\end{matrix}\right\}N}^{\text{Methylia.}} + \overbrace{2\,(KO,\ CO_2)}^{\text{Carb. Potash.}}.$$

$$\overbrace{H_3\,(C_2H_3)\ N_2C_2O_2}^{\text{Methyl-urea.}} + 2(KO,\ HO) = \overbrace{\left.\begin{matrix}C_2H_3\\H_2\end{matrix}\right\}N}^{\text{Methylia.}} + H_3N + 2\,(KO,\ CO_2).$$

Hofmann (*Phil. Trans.*, 1850) found shortly afterwards that these bases may also be produced directly from ammonia, by acting upon this alkali by means of the hydriodic, or the hydrobromic ethers of the different alcohols. He obtained this result by enclosing, in a long sealed tube, a mixture of a concentrated alcoholic solution of ammonia, and the bromide, or the iodide derived from the alcohol which he wished to examine. When this mixture was heated for some hours in a water-bath, combination occurred, and an iodide, or bromide, of the new base was formed.

Thus, when iodide of ethyl is made to act upon a solution of ammonia, the following change occurs:—

$$\overbrace{H_3N}^{\text{Ammonia.}} + \overbrace{C_4H_5I}^{\text{Iodide of Ethyl.}} = \overbrace{\left.\begin{matrix}C_4H_5\\H_2\end{matrix}\right\}N, HI.}^{\text{Hydriodate of Ethylia.}}$$

When the result of this reaction is distilled with hydrate of potash, ethylia is liberated, and iodide of potassium is formed. Now, if ethylia be submitted in a sealed tube to a fresh portion of iodide of ethyl, a second equivalent of hydrogen will be removed, and an additional equivalent of ethyl will be substituted for it, whilst the hydriodate of a new base (diethylia) is formed:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\H_2\end{matrix}\right\}N}^{\text{Ethylia.}} + \overbrace{C_4H_5I}^{\text{Iodide of Ethyl.}} = \overbrace{\left.\begin{matrix}2\,(C_4H_5)\\H\end{matrix}\right\}N, HI;}^{\text{Hydriodate of Diethylia.}}$$

and if the hydriodate of diethylia be submitted to distillation with hydrate of potash, diethylia itself will be liberated. This base may in its turn be treated with a fresh portion of iodide of ethyl, and so the third equivalent of hydrogen may be displaced by a third equivalent of ethyl, yielding a salt which, when distilled with potash, furnishes a third base, triethylia $3\ (C_4H_5)N$.

Each of the alcohols may be made to furnish bases corresponding to each of the foregoing ethyl bases; thus, by similar methods, a mixture of iodide of methyl and ammonia can easily be made to yield methylia, dimethylia, and trimethylia; and from iodide of amyl, amylia, diamylia, and triamylia, may be formed. These bases are all homologous with ammonia, which they closely resemble in properties. But the action of iodide of ethyl does not stop even here, for it is possible, by its means, to obtain a fourth series of bases homologous with the hypothetical body ammonium. (Hofmann, *Phil. Trans.*, 1851.) If, for example, a quantity of triethylia be heated in a tube with an additional dose of iodide of ethyl, the two bodies enter into combination, and a compound, $4\ (C_4H_5)\ N, I$, analogous to iodide of ammonium (H_4N, I), is formed; all the 4 equivalents of hydrogen in the ammonium having been displaced by ethyl:—

$$\overbrace{3\,(C_4H_5)\,N}^{\text{Triethylia.}} + \overbrace{C_4H_5I}^{\text{Iodide of Ethyl.}} = \overbrace{4\,(C_4H_5)\,N, I.}^{\text{Iodide of Tetrethylium.}}$$

The iodide thus obtained is a crystalline substance. It is not possible to obtain the base tetrethylium, $4\ (C_4H_5)N$, in a separate form; since, like ammonium, it immediately undergoes decomposition; but if the iodide be treated with freshly precipitated oxide of silver, double decomposition ensues, iodide of silver is formed, and the *hydrated oxide* of tetrethylium is liberated:—

$$\overbrace{4(C_4H_5)N, I}^{\text{Iodide of Tetrethylium.}} + AgO, HO = AgI + \overbrace{4(C_4H_5)N, O, HO}^{\text{Hydrated Oxide of Tetrethylium.}}.$$

It might have been anticipated that, under these circumstances, tetrethylium should have been resolved into triethylia and alcohol, just as ammonium becomes broken up into ammonia and water when similarly treated: thus, since

$$H_4NI + AgO, HO \text{ yields } AgI + \left.\begin{matrix}H\\H\end{matrix}\right\} O_2 + H_3N; \text{ so also}$$

$$\overbrace{4(C_4H_5)NI}^{\text{Iodide of Tetrethylium.}} + AgO, HO \text{ should become } AgI + \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\} O_2}^{\text{Alcohol.}} + 3\overbrace{(C_4H_5)N}^{\text{Triethylia.}};$$

but such is not the case; the new compound is very stable, and on evaporation of the solution, the hydrate of the new base may be obtained in crystals, which, like those of hydrate of potash, absorb water and carbonic acid from the atmosphere, and possess the caustic action of potash, combined with a bitter taste like that of quinia. This base forms the type of a numerous class, which are analogous to it both in composition and in properties. Hydrated oxide of tetrethylium, in common with many others like it, such as the hydrated oxide of tetramethylium ($4(C_2H_3)NO, HO$), is sufficiently powerful to saponify the oils and to precipitate the metallic oxides from their salts, just as potash does. It forms crystallizable salts. These bases differ in a marked manner from such bases as ethylia, diethylia, and triethylia, all of which, like ammonia, are volatile without decomposition. The hydrated oxide of tetrethylium, and others which resemble it, however, cannot be volatilized without undergoing decomposition, in which case they are converted into water, a hydrocarbon homologous with olefiant gas, and a volatile alkali corresponding to triethylia:—

$$\overbrace{4(C_4H_5)NO, HO}^{\text{Hydrated Oxide of Tetrethylium.}} = 2HO + \overbrace{C_4H_4}^{\text{Olefiant Gas.}} + 3\overbrace{(C_4H_5)N}^{\text{Triethylia.}}.$$

Ammonia is thus capable of originating two classes of bases, one set being volatile, and corresponding in properties to ammonia itself; the other set fixed, resembling hydrate of potash in properties, and corresponding to hydrated oxide of ammonium.

If *phenylia* ($C_{12}H_5, H_2N$), or aniline, as it is commonly termed, be employed instead of ammonia, a corresponding series of bases may be obtained from it, in which the two equivalents of hydrogen may be successively displaced by one of the alcohol radicles; and finally, the compound may be converted into an ammonium base by the action of another equivalent of iodide of ethyl; thus aniline (or phenylia) $\left.\begin{matrix} C_{12}H_5 \\ H \\ H \end{matrix}\right\} N$, becomes, when treated with iodide of ethyl, successively, 1. ethyl-phenylia $\left.\begin{matrix} C_{12}H_5 \\ C_4H_5 \\ H \end{matrix}\right\} N$; 2. diethyl-phenylia $\left.\begin{matrix} C_{12}H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right\} N$; 3. and finally, hydrated oxide of triethylphenylium $\left.\begin{matrix} C_{12}H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right\} N, O, HO$.

Dr. Hofmann, in the further investigation of this remarkable method of preparing artificial bases, found that each of the three equivalents of hydrogen in ammonia might be displaced by a different alcohol radicle. Thus it was possible to obtain, first, methylia, by the action of iodide of methyl upon ammonia; then by acting upon methylia with iodide of ethyl, the compound methyl-ethylia (corresponding to diethylia) was formed,

$$\left.\begin{matrix} C_2H_3 \\ H \\ H \end{matrix}\right\} N + \overbrace{C_4H_5I}^{\text{Iodide of Ethyl.}} = \left.\begin{matrix} C_2H_3 \\ C_4H_5 \\ H \end{matrix}\right\} N, HI;$$

and on distilling this hydriodate of methyl-ethylia with hydrate of potash, the new base was liberated. Now, if methyl-ethylia were treated with iodide of amyl, a compound corresponding to triethylia was formed, but containing, in the place of the three equivalents of ethyl, 3 different alcohol radicles, thus:—

$$\overbrace{\left.\begin{matrix} C_2H_3 \\ C_4H_5 \\ H \end{matrix}\right\} N, HI}^{\text{Hydriodate of Methyl-ethylia.}} + \overbrace{C_{10}H_{11}I}^{\text{Iodide of Amyl.}} = \overbrace{\left.\begin{matrix} C_2H_3 \\ C_4H_5 \\ C_{10}H_{11} \end{matrix}\right\} N, HI.}^{\text{Hydriodate of Methyl-ethyl-amylia.}}$$

Hofmann has even succeeded in obtaining an ammonium base, derived from aniline, containing 4 different hydrocarbon radicles, and to which the unwieldy name of hydrated oxide of methyl-ethyl-amylo-phenylium must be assigned:—

$$\left.\begin{matrix} C_2H_3 \\ C_4H_5 \\ C_{10}H_{11} \\ C_{12}H_5 \end{matrix}\right\} N, O, HO = C_{28}H_{24}NO, HO.$$

It, of course, will not be overlooked that if the ordinary salts of ammonia are considered to be compounds of ammonium, the salts of all the bases derived from ammonia ought to be considered from the same point of view:—If hydriodate of ammonia be regarded as iodide of ammonium, hydriodate of ethylia should be iodide of ethylium, and the composition and nomenclature of the ethyl bases would be simply translated thus; no hydriodates of the ammonium bases are known:—

$$\overbrace{(C_4H_5)\,H_2\,N,\,HI}^{\text{Hydriodate of Ethylia.}} \quad = \quad \overbrace{(C_4H_5)\,H_3N,\,I}^{\text{Iodide of Ethylium.}}$$

$$\overbrace{2(C_4H_5)\,H,\,N,\,HI}^{\text{Hydriodate of Diethylia.}} \quad = \quad \overbrace{2(C_4H_5)\,H_2N,\,I}^{\text{Iodide of Diethylium.}}$$

$$\overbrace{3(C_4H_5)\,N,\,HI}^{\text{Hydriodate of Triethylia.}} \quad = \quad \overbrace{3(C_4H_5)\,HN,\,I}^{\text{Iodide of Triethylium.}}$$

$$\underset{\text{(wanting.)}}{\text{Hydriodate of Oxide of Tetrethylium.}} \qquad \overbrace{4(C_4H_5)\,N,\,I.}^{\text{Iodide of Tetrethylium.}}$$

In this work, however, for the sake of marking the distinction between the volatile and the fixed bases, the termination *ium* will be reserved for such bases as are formed upon the type of oxide of ammonium.

An important circumstance, in relation to the molecular constitution of ammonia, was elicited in the course of these investigations. Let the three equivalents of hydrogen in ammonia be represented by the letters h, H and H; and let $\left.\begin{matrix}h\\ \mathrm{H}\\ H\end{matrix}\right\}\mathrm{N}$ = ammonia:—it might be supposed that the three different equivalents of hydrogen h, H, and H, in the molecule of ammonia, might each have a different function to perform in the alkaline group. Suppose, then, that a derivative base were formed, in which the equivalent of hydrogen h were replaced by a radicle called X, forming a new base $\left.\begin{matrix}\mathrm{X}\\ \mathrm{H}\\ H\end{matrix}\right\}\mathrm{N}$; the other equivalents of hydrogen, H and H, admit of being displaced respectively by other radicles, Y and Z. Suppose, for example, that X represents phenyl ($C_{12}H_5$), Y, amyl, and Z, ethyl; the question is, whether the same compound will be formed indifferently when amyl is substituted for H, and ethyl for H, or when ethyl supplies the place of H, and amyl of H. Whether, in fact, there will be any perceptible difference if the compound be obtained in the form of $\left.\begin{matrix}X\\Y\\Z\end{matrix}\right\}N$; or of $\left.\begin{matrix}X\\Z\\Y\end{matrix}\right\}N$. To decide this point Dr. Hofmann carefully compared the properties of amyl-ethylo-phenylia ($C_{22}H_{17}N$), prepared by acting upon amylo-phenylia $\left.\begin{matrix}C_{12}H_5\\C_{10}H_{11}\\H\end{matrix}\right\}N$, by bromide of ethyl ($C_4H_5Br$), which would yield $\left.\begin{matrix}C_{12}H_5\\C_{10}H_{11}\\C_4H_5\end{matrix}\right\}N$, with the compound ethyl-amylo-phenylia $\left.\begin{matrix}C_{12}H_5\\C_4H_5\\C_{10}H_{11}\end{matrix}\right\}N$, formed by decomposing ethylo-phenylia $\left.\begin{matrix}C_{12}H_5\\C_4H_5\\H\end{matrix}\right\}N$, with bromide of amyl ($C_{10}H_{11}Br$); but the two substances comported themselves alike in all respects. The two bodies thus obtained are, therefore, not only isomeric, but identical, and the functions of the two equivalents of hydrogen H and *H* in ammonia must be similar. The case, however, is very different if alkalies be compared together which have the same empirical formulæ, but which have been produced by the substitution of dissimilar alcohol radicles.

In order to render this evident, it will be necessary to allude to a series of bases obtained by a totally different method. The researches of chemists have gradually proved the existence of a series of hydrocarbons which are homologous with benzole ($C_{12}H_6$), and each of these hydrocarbons when treated first with nitric acid and subsequently by hydrosulphate of ammonia, or some other suitable reducing agent, has yielded its corresponding base, so that we are now in possession of the following hydrocarbons and their derived bases:—

Hydrocarbons (C_nH_{n-6})		Base ($C_nH_{n-5}N$)	
1. Benzole	$C_{12}H_6$	1. Aniline	$C_{12}H_7N$
2. Toluole	$C_{14}H_8$	2. Toluidine . . .	$C_{14}H_9N$
3. Xylole	$C_{16}H_{10}$	3. Xylidine . . .	$C_{16}H_{11}N$
4. Cumole	$C_{18}H_{12}$	4. Cumidine . . .	$C_{18}H_{13}N$
5. Cymole	$C_{20}H_{14}$	5. Cymidine . . .	$C_{20}H_{15}N$

Toluidine has the same composition as methylaniline; xylidine as ethylaniline, and cumidine as methylethylaniline. These pairs of substances are, however, only metameric, they are not identical. Toluidine is a fusible crystalline solid, which boils at 388°, and yields stable, sparingly soluble salts, with most of the acids, including a beautiful crystallizable double salt with chloride of platinum. Methylaniline is an oily liquid which boils at 377°; while its salts are distinguished by their solubility and the facility with which they are decomposed; aniline being reproduced; its platinum salt is of a pale yellow colour, and begins to blacken almost immediately after its formation: whilst toluidine does not yield aniline under any known circumstances. The properties of cumidine and ethylaniline though both are liquid at ordinary temperatures are not less distinct. Again, it is possible to introduce an equivalent of ethyl into toluidine; one of the equivalents of hydrogen which this base contains being readily eliminated when the alkali is treated with iodide of ethyl. The ethylo-toluidine thus obtained is a third alkali isomeric or metameric with cumidine, yet possessed of properties quite distinct from it. Thus it is evident that three different alkaloids are already known, all of which possess the empirical formula $C_{18}H_{13}N$; and there is no doubt that besides these, three other bases each having the same empirical formula, and the same combining equivalent could readily be obtained; yet each of these new bases would differ in constitution from the foregoing bases and from each other; they would also probably be found mutually to differ in properties. The first of these new bases (methylo-xylidine) might be formed by inserting an equivalent of methyl into xylidine; the second (dimethylo-toluidine) would be formed by substituting 2 equivalents of methyl in toluidine for 2 equivalents of hydrogen; the third, trityl-aniline, would be obtained by combining trityl (C_6H_7), the radicle of tritylic alcohol (C_6H_7O, HO), with aniline. The six bases metameric with cumidine would, therefore, have the composition which is represented in the following table:—

Known bases.	*Bases not yet formed.*
Cumidine. $\overbrace{\left.\begin{array}{c}C_{18}H_{11}\\ H\\ H\end{array}\right\}}N$	Methylo-xylidine. $\overbrace{\left.\begin{array}{c}C_{16}H_{9}\\ C_{2}\,H_{3}\\ H\end{array}\right\}}N$
Ethylo-toluidine. $\overbrace{\left.\begin{array}{c}C_{14}H_{7}\\ C_{4}\,H_{5}\\ H\end{array}\right\}}N$	Dimethylo-toluidine. $\overbrace{\left.\begin{array}{c}C_{14}H_{7}\\ C_{2}\,H_{3}\\ C_{2}\,H_{3}\end{array}\right\}}N$
Methyl-ethyl-aniline. $\overbrace{\left.\begin{array}{c}C_{12}H_{5}\\ C_{4}\,H_{5}\\ C_{2}\,H_{3}\end{array}\right\}}N$	Trityl-aniline. $\overbrace{\left.\begin{array}{c}C_{12}H_{5}\\ C_{6}\,H_{7}\\ H\end{array}\right\}}N$

The manner in which toluidine and other bases not derived from the alcohols admit of being attacked by the hydriodic and hydrobromic ethers shows that the action of these ethers upon the different bases affords a most important means of examining and dissecting these various compounds; and it has been found to be applicable to organic bases both of natural and artificial origin. Within the few years that have elapsed since Dr. Hofmann first showed the applicability of these reagents to this purpose, extensive use has already been made of them in such examinations.

(1028) *Hofmann's Classification of Organic Bases.*—Hofmann has proposed to classify the various new bases which may be produced by these methods of substitution, under the heads of *amidogen, imidogen, nitrile,* and *ammonium* bases. Amidogen bases are those which may be regarded as still retaining 2 equivalents of the hydrogen of the original ammonia, one equivalent only of hydrogen having been displaced by a hydrocarbon. In the imidogen bases the substitution has proceeded a step further; one equivalent of hydrogen of the original ammonia only being left; whilst in the nitrile bases none of the hydrogen of the ammonia remains. In the ammonium bases a fourth equivalent of a hydrocarbon is superadded, and takes the place of the fourth equivalent theoretically assigned to ammonium. All the ammonium bases while separated from their salts contain at least one equivalent of water, and they are therefore only known in the form of hydrates. The table on the following page will afford an illustration of the mode of classifying the different bases upon this principle.

There can be no doubt that in certain cases the vegetable alkaloids (1059) as they exist in the plant, are formed upon the type of ammonia; though in the present state of our knowledge upon this subject we are far from warranted in drawing the general conclusion that such is their constitution in all instances. The two bases last mentioned in the table, viz., conia and nicotia, are the natural volatile alkalies contained respectively in hemlock and in tobacco. On treating conia with iodide of methyl, two compounds were formed, the simpler of which may be considered as a nitrile base, and the more complicated as an ammonium base; conia itself being regarded as an imidogen base in which the group $(C_{16}H_{14})$ has displaced 2 equivalents of hydrogen, and this view is indicated in the notation by the marks (″) which follow the hydrocarbon. It is possible that this hydrocarbon may itself be composed of (C_8H_7) (C_8H_7), so that each equivalent of hydrogen may have been displaced by the group (C_8H_7). Nicotia, on the other hand, must be regarded as a nitrile base, in which the 3 equivalents of hydrogen in ammonia have been displaced by the group $(C_{10}H_7)$,

Ammonia-Bases.	Amidic, or Amidogen-Bases.	Imidic, or Imidogen Bases.	Nitrile Bases.	Bases analogous to Hydrated Oxide of Ammonium.
Ammonia (H$_3$N) $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$	Methylia . (C$_2$H$_5$N) $\left.\begin{matrix}C_2H_3\\H\\H\end{matrix}\right\}N$	Dimethylia . (C$_4$H$_7$N) $\left.\begin{matrix}C_2H_3\\C_2H_3\\H\end{matrix}\right\}N$	Trimethylia . . (C$_6$H$_9$N) $\left.\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}N$	Hydrated oxide of tetramethylium (C$_8$H$_{12}$NO, HO) $\left.\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}NO, HO$
	Ethylia . (C$_4$H$_7$N) $\left.\begin{matrix}C_4H_5\\H\\H\end{matrix}\right\}N$	Diethylia . . (C$_8$H$_{11}$N) $\left.\begin{matrix}C_4H_5\\C_4H_5\\H\end{matrix}\right\}N$	Triethylia . . (C$_{12}$H$_{15}$N) $\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N$	Hydrated oxide of tetrethylium (C$_{16}$H$_{20}$NO, HO) $\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}NO, HO$
	Amylia . (C$_{10}$H$_{13}$N) $\left.\begin{matrix}C_{10}H_{11}\\H\\H\end{matrix}\right\}N$	Diamylia . . (C$_{20}$H$_{23}$N) $\left.\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\\H\end{matrix}\right\}N$	Triamylia . . (C$_{30}$H$_{33}$N) $\left.\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right\}N$	Hydrated oxide of tetramylium (C$_{40}$H$_{44}$NO, HO) $\left.\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\\C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right\}NO, HO$
Phosphuretted Hydrogen (H$_3$P) $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}P$	Aniline . (Phenylia) C$_{12}$H$_7$N) $\left.\begin{matrix}C_{12}H_5\\H\\H\end{matrix}\right\}N$	Ethylphenylia, or ethylaniline (C$_{16}$H$_{11}$N) $\left.\begin{matrix}C_{12}H_5\\C_4H_5\\H\end{matrix}\right\}N$	Diethylphenylia, or Diethylaniline . (C$_{20}$H$_{15}$N) $\left.\begin{matrix}C_{12}H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N$	Hydrated oxide of triethylophenylium (C$_{24}$H$_{20}$NO, HO) $\left.\begin{matrix}C_{12}H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}NO, HO$
		Methylphenylia, or methylaniline (C$_{14}$H$_9$N) $\left.\begin{matrix}C_{12}H_5\\C_2H_3\\H\end{matrix}\right\}N$	Methyl-ethyl-phenylia, or methyl-ethyl.aniline (C$_{18}$H$_{13}$N) $\left.\begin{matrix}C_{12}H_5\\C_4H_5\\C_2H_3\end{matrix}\right\}N$	Hydrated oxide of methyl-ethyl-amylophenylium (C$_{28}$H$_{24}$NO, HO) $\left.\begin{matrix}C_{12}H_5\\C_{10}H_{11}\\C_4H_5\\C_2H_3\end{matrix}\right\}NO, HO$
Arseniuretted Hydrogen (H$_3$As) $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}As$			Methyl-ethyl-amylia (C$_{16}$H$_{19}$N) $\left.\begin{matrix}C_{10}H_{11}\\C_4H_5\\C_2H_3\end{matrix}\right\}N$	Hydrated oxide of methyl-diethyl-amylium (C$_{20}$H$_{24}$NO, HO) $\left.\begin{matrix}C_{10}H_{11}\\C_4H_5\\C_4H_5\\C_2H_3\end{matrix}\right\}NO, HO$
	Chlorophenylia, or chloraniline (C$_{12}$H$_6$ClN) $\left.\begin{matrix}C_{12}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.\\H\\H\end{matrix}\right\}N$	Ethylochlorophenylia, or ethylochloraniline (C$_{16}$H$_{10}$ClN) $\left.\begin{matrix}C_{12}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.\\C_4H_5\\H\end{matrix}\right\}N$	Diethylochlorophenylia, or diethylochloraniline (C$_{20}$H$_{14}$ClN) $\left.\begin{matrix}C_{12}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.\\C_4H_5\\C_4H_5\end{matrix}\right\}N$	
Antimoniuretted Hydrogen (H$_3$Sb)? $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}Sb$	Toluidine . (C$_{14}$H$_9$N) $\left.\begin{matrix}C_{14}H_7\\H\\H\end{matrix}\right\}N$	Ethylotoluidine (C$_{18}$H$_{13}$N) $\left.\begin{matrix}C_{14}H_7\\C_4H_5\\H\end{matrix}\right\}N$	Dimethylotoluidine (C$_{18}$H$_{13}$N) $\left.\begin{matrix}C_{14}H_7\\C_2H_3\\C_2H_3\end{matrix}\right\}N$	
		Conia . . . (C$_{16}$H$_{15}$N) $\left.\begin{matrix}(C_{16}H_{14}'')\\H\end{matrix}\right\}N$	Methyl-conia . (C$_{18}$H$_{17}$N) $\left.\begin{matrix}(C_{16}H_{14}'')\\C_2H_3\end{matrix}\right\}N$	Hydrated oxide of methyl-ethyl-conium C$_{22}$H$_{22}$NO, HO) $\left.\begin{matrix}(C_{16}H_{14})''\\C_4H_5\\C_2H_3\end{matrix}\right\}NO, HO$
			Nicotia . . . (C$_{10}$H$_7$N) (C$_{10}$H$_7$''') N	Hydrated oxide of ethyl-nicotium (C$_{14}$H$_{12}$NO, HO) $\left.\begin{matrix}(C_{10}H_7)'''\\C_4H_5\end{matrix}\right\}NO, HO$

which, therefore, as being equivalent in combining power to H_3, is marked $(C_{10}H_7)'''$. There are various ways in which it is conceivable that this hydrocarbon may be composed, such as (C_4H_2, C_3H_3, C_3H_2) or (C_4H_2, C_4H_2, C_2H_3), but there is no reason for preferring any one of these possible combinations, nor is there any proof that the compound ($C_{10}H_7$) is to be considered as divisible into other hydrocarbons. Anderson and Gerhardt have each suggested that there may exist in organic bases and in other compounds more or less analogous to them, monobasic, dibasic, and tribasic hydrocarbons, or rather hydrocarbons respectively equivalent to H, H_2, and H_3, just as chemists have long been in the habit of admitting the existence of monobasic, dibasic, and tribasic acids (460), requiring for saturation oxides containing M, M_2, or M_3 (M representing hydrogen, or a metal). For the further prosecution of this subject the reader is referred to the papers of Anderson (*Trans. Roy. Soc. Edinburgh,* xxi. 231); and Gerhardt and Chiozza (*Ann. de Chimie,* III., xlvi. 167).

(1029) *Bases obtained from phosphuretted, arseniuretted, and antimoniuretted hydrogen.*—The first column of the table of bases just given includes three substances which do not possess basic properties, but which present the closest analogy in composition with ammonia; viz., phosphuretted, arseniuretted, and antimoniuretted hydrogen. The latter has never been isolated in a state of sufficient purity to admit of a satisfactory analysis; but there can be little doubt that it possesses the composition assigned to it in the table: since when the gas, diluted as it always is with hydrogen, is transmitted through a solution of nitrate of silver, an antimonide of silver having the composition Ag_3Sb is precipitated, and it would not be easy to account for the formation of this compound if the gas had any other composition:—

$$3\ (AgO, NO_5) + H_3Sb = 3\ (HO, NO_5) + Ag_3Sb.$$

Phosphuretted, arseniuretted, and antimoniuretted hydrogen may therefore be considered each to contain 3 equivalents of hydrogen, and one equivalent of their characteristic components; and they may be looked upon as analogues, or representatives of ammonia, in which the nitrogen has been displaced respectively by phosphorus, arsenic, and antimony. Widely as these three elements differ from nitrogen in their separate form, they yet exhibit a considerable analogy with it in their mode of entering into combination; all three of them forming not only corresponding compounds with hydrogen, but, like nitrogen, all of them yield with oxygen powerful acids which contain 5 equivalents of oxygen; the anhydrides being respectively—

Nitric anhydride	NO_5
Phosphoric	PO_5
Arsenic	AsO_5
Antimonic	SbO_5.

Neither arseniuretted nor antimoniuretted hydrogen exhibits any basic properties, and the only indication of basic power in the case of phosphuretted hydrogen consists in the formation of volatile crystalline bodies with hydrobromic and hydriodic acids (376); yet it has been shown by P. Thénard (*Comptes Rendus*, xxi. 144, xxv. 892), that if the hydrogen of phosphuretted hydrogen be displaced by methyl or by ethyl, powerful bases may be procured, formed upon the type of ammonia, but containing phosphorus instead of nitrogen, and ethyl or methyl in the place of hydrogen. Hofmann and Cahours have recently investigated these compounds more minutely, and have described a method by which they may be obtained with certainty. The process introduced by the chemists last named, for the preparation of these phosphorized bases consists in the action of terchloride of phosphorus (PCl_3) upon zinc-methyl, zinc-ethyl, &c., when chloride of zinc is formed, and the new base is produced. These bases have a most offensive odour, and many of them when mixed with atmospheric air, or oxygen, take fire, especially if the temperature be slightly raised. But not only may phosphorized bases $3\,(C_2H_3)P$, $3\,(C_4H_5)P$, $3\,(C_{10}H_{11})P$, &c., analogous to ammonia be formed, but by treating these new bases with iodide of ethyl, of methyl, or of amyl, iodides of ammonium-bases analogous to that of tetrethylium may be obtained; and by the action of oxide of silver upon these iodides, hydrates of the new ammonium-bases may be procured. Both arsenic and antimony form with ethyl and methyl, and the other alcohol radicles, compounds which combine with oxygen, and possess basic properties as powerful as those of many of the metallic oxides (1037, 1043).

(1030) METHYLIA; *methylamine* ($C_2H_5N = C_2H_3, H_2N$), *Sp. gr. of vapour* 1·08.—This body is gaseous under ordinary circumstances, but may be condensed by a freezing mixture to a very mobile liquid, which is not solidified by exposure to a bath of solid carbonic acid and ether. It is colourless, and has an intensely pungent odour of ammonia, and an extremely powerful alkaline reaction, producing dense white fumes when exposed to the vapour of hydrochloric acid; but it is distinguished from ammonia by its ready inflammability; it burns with a yellowish livid flame, and furnishes carbonic acid, water, and nitrogen, accompanied, if the supply of air be insufficient, with traces of cyanogen or of hydrocyanic acid. Methylia is more soluble in water than any other known gas; at 55° water dissolves 1150 times its bulk, forming a powerfully alkaline solution with a very pungent ammoniacal odour, and a strongly caustic action upon the skin; when boiled the alkali is expelled in the gaseous form. Solution of methylia acts upon solutions of the metallic salts, as ammonia would do, dissolving the precipitated oxides of zinc, silver, and copper; in the latter case forming a deep blue liquid. The oxides of cadmium, of cobalt, and of nickel, are precipitated by methylia, but are not redissolved by it.

When methylia is passed through a porcelain tube heated to redness, it is decomposed; hydrocyanate of ammonia, and a gaseous mixture of hydrocyanic acid, hydride of methyl, and free hydrogen being formed:—

$$3\ \overbrace{(C_2H_5N)}^{\text{Methylia.}} = \overbrace{H_3N,\ HC_2N}^{\text{Hydrocy. Ammon.}} + HC_2N + \overbrace{C_2H_3,\ H}^{\text{Hydride of Methyl.}} + 6\ H.$$

If potassium be heated in gaseous methylia, cyanide of potassium is formed, and hydrogen is liberated; $C_2H_5N + K = K,C_2N + 5\ H$.

Preparation.—Methylia is readily obtained by distilling the carefully dried hydrochlorate of the base with twice its weight of quicklime. The operation should be performed in a long tube, the lower half of which is filled with the mixture, and the upper half with hydrate of potash, in order to dry the gas completely; it may be collected in jars over mercury. Hydrochlorate of methylia is best obtained for this purpose by distilling cyanurate of methyl with hydrate of potash (1008), and saturating the distillate with hydrochloric acid; the residue when evaporated to dryness may be dissolved in boiling absolute alcohol, from which on cooling it crystallizes in large iridescent foliated deliquescent crystals: at a temperature a little above 212° it fuses, and when heated in an open vessel it volatilizes in dense white clouds, which may be condensed unchanged. This salt does not yield any amalgam similar to that of ammonium when decomposed by the voltaic battery in contact with mercury, nor when its concentrated solution is mixed with an amalgam of potassium.

Most of the salts of methylia are very soluble in water. Its hydrochlorate forms with bichloride of platinum a soluble compound, crystallizing in golden yellow scales, which are insoluble in alcohol.

Trimethylia [illegible] $C_6H_9N = 3(C_2H_3),N$).—This alkali, wh
[illegible] propylia (C_6H_7, H_2N), is found in consider
[illegible] herrings. It has an extremely po
[illegible] odour. It is also obtained by distilli
[illegible] hydrate of potash: and it imparts to the c
its peculiar odour. Trimethylia is a very vol
[illegible] and emits an inflammable v
[illegible] water. Iodide of methyl immediately convert
[illegible] crystals of iodide of tetramethylium.

Tetramethylium.—The iodide of this base is the pri
[illegible] by heating iodide of methyl in excess with
[illegible] in wood spirit or in alcohol. Since the iodi
[illegible] sparingly soluble in cold water, it may
[illegible] accompanying hydriodates of methylia, dimethy
[illegible] by crystallization from boiling water. When t
[illegible] precipitated oxide of silver, iodide of silver is f
[illegible] hydrated oxide of tetramethylium ($4(C_2H_3)NO, HO$
[illegible] it may be obtained by evaporation *in* v
[illegible] crystals which are deliquescent, and a
[illegible] Its salts crystallize well, particularly t
which forms long brilliant needles. The double c
platinum and tetramethylium ($C_8H_{12}NCl, PtCl_2$), crys
[illegible] orange-coloured magnificent octohedra.

When the hydrated oxide of tetramethylium is treat
[illegible] quantity of iodide of methyl, no further comb
methyl with the base occurs; but double decompositio
iodide of tetramethylium is formed, and wood spirit libe

$$\underbrace{4(C_2H_3)NO,HO}_{\text{Oxide of Tetramethylium.}} + \underbrace{C_2H_3I}_{\text{Iodide of Methyl.}} = \underbrace{C_2H_3O,HO}_{\text{Wood Spirit.}} + \underbrace{4(C_2}_{\text{Iodide of T}}$$

(1031) Ethylia, *Ethylamine* ($C_4H_7N = C_4H_5, H_2N$),
liquid 0·696, *of vapour* 1·594.—This base constitutes a ve
colourless liquid, which boils at 65°·6 F. emitting an in
vapour of a pungent ammoniacal odour. It is misc
water in all proportions, but by prolonged boiling the wh
ethylia may be expelled. Ethylia produces results with
of metallic salts exactly similar to those of methylia, fro
however, it may be distinguished by the power poss
ethylia of dissolving recently precipitated alumina. W
proposed to take advantage of this property as a means
rating alumina from oxide of iron, in the operations of
Ethylia displaces ammonia from its salts if evapora

them. It yields dense white fumes with vapours of hydrochloric acid.

Ethylia may be prepared in a manner similar to that directed for methylia, by acting upon cyanic or cyanuric ether with hydrate of potash. It may also be obtained by acting upon iodide of ethyl with ammonia, in which case hydriodate of ethylia is formed; or by heating a mixture of ether with muriate of ammonia in a sealed tube (Hofmann). The salts of ethylia do not generally crystallize with facility; they are soluble in water and in alcohol. The hydrochlorate forms colourless plates, which are fusible at 169°. The sulphate is deliquescent, and since it is soluble in alcohol it may readily be separated from sulphate of ammonia, which is insoluble in this menstruum. The double salt with bichloride of platinum (C_4H_7N, HCl, $PtCl_2$) crystallizes in yellow octohedra.

Diethylia ($C_8H_{11}N = 2\ C_4H_5$, HN), is a colourless, volatile, inflammable liquid, powerfully alkaline, and very caustic. It boils at 134°·6. It may be obtained by treating ethylia with iodide of ethyl in the manner already described (1027).

Triethylia ($C_{12}H_{15}N = 3\ C_4H_5$, N) is also a soluble, volatile, and powerful base, which forms a beautiful orange double salt with bichloride of platinum, crystallizing in large rhombic tables [$3\ (C_4H_5)$ N, HCl, $PtCl_2$]. Triethylia may be obtained from the foregoing base by the action of iodide of ethyl upon it. The salts of tetrethylium are procured by continuing the action of iodide of ethyl upon triethylia.

The *hydrated oxide of tetrethylium* is a powerful base, perfectly analogous to the corresponding compound of tetramethylium. It may be obtained in solution by treating the iodide of tetrethylium with oxide of silver. If this solution be allowed to evaporate *in vacuo* over sulphuric acid, the base forms long hair-like needles, which are very deliquescent, and absorb carbonic acid with great avidity. A strong solution of the base may be boiled without undergoing decomposition, but if evaporated to dryness over the water bath it becomes decomposed as soon as the water is nearly all expelled. A solution of the base acts powerfully upon the cuticle, and it saponifies the fats as readily as potash, forming soft soaps. The oxide of tetrethylium is not liberated from its iodide by the action of potash; on adding a solution of potash to one of the iodide of the base, a crystalline mass of the pure iodide of tetrethylium is separated, as it is less soluble in alkaline liquids than in pure water: even when boiled with the concentrated solution of potash for some hours, no decomposition is effected; but it is decomposed with facility by the salts of silver, or by the freshly precipitated oxide of silver. Analogous reactions with potash and oxide of silver are found to occur with a large number of other ammonium bases.

Bases derived from other Alcohols.

(1032) *Tritylia* or *propylamine* ($C_6H_7H_2N$), is isomeric with trimethylia; it is one of the bases obtained by Anderson during the destructive distillation of bones; and the same chemist has likewise procured from this liquid another base, which he termed *petinine*, but which corresponds to *tetrylia* or *butyria* (C_8H_9, H_2N), the alkali of tetrylic alcohol; both these bases are volatile liquids.

A series of bases corresponding to those from methylic and ethylic alcohols, has also been obtained from fousel oil. Their basic powers are smaller than those of the ethyl and methyl series, and they present no particular points of interest. *Amylia* ($C_{10}H_{11}H_2N$) is a very light colourless liquid which boils at 203° F., and is of sp. gr. 0·750. Its salts crystallize readily.

The alcohol from castor oil (octylic alcohol) also yields a well-marked base, *octylia* or *caprylia* ($C_{16}C_{17}H_2N$); and even the alcohol of palmitic acid, ethal, has been made to yield a compound ammonia in which all the three equivalents of hydrogen have given place to the hydrocarbon of ethal, thus forming *tricetylia* $3\,(C_{32}H_{33})\,N$, which crystallizes in white fusible needles, freely soluble in boiling alcohol. Its salts are not soluble in water, but they crystallize readily from boiling alcohol and from ether.

§ VIII. METALLIC DERIVATIVES OF THE ALCOHOLS.

(1033) It has been already stated (986-7), that when sodium or potassium is made to act upon one of the alcohols, hydrogen is eliminated, and a compound is formed, which presents a certain analogy with the ordinary salts of sodium or of potassium; if we compare the action of sodium upon alcohol, and upon menohydrated acetic acid, the results of the reaction may be thus represented:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} + Na = \overbrace{\left.\begin{matrix}C_4H_5\\Na\end{matrix}\right\}O_2}^{\text{Sodium Alcohol.}} + H$$

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2}^{\text{Acetic Acid.}} + Na = \overbrace{\left.\begin{matrix}C_4H_3O_2\\Na\end{matrix}\right\}O_2}^{\text{Acetate of Soda.}} + H$$

We have seen that when such compounds are acted upon by the ethers of the hydracids, either simple or double ethers are formed from them by a process of substitution or double decomposition:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\Na\end{matrix}\right\}O_2}^{\text{Alcohol.}} + \overbrace{C_4H_5I}^{\text{Iodide of Ethyl.}}, \text{ becoming } \overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2}^{\text{Ether.}} + \overbrace{NaI}^{\text{Iodide of Sodium.}}.$$

Within the last few years, however, a series of compounds has been obtained in which a metallic element enters still more intimately into the composition of the base of the alcohol. The first substance of this class that was carefully investigated was kakodyl (C_4H_6As); and this body was shown by the masterly researches of Bunsen, to perform the part of a compound metal. At Bunsen's instigation, Frankland undertook a series of researches, which led to the discovery of a number of new bodies more or less analogous to kakodyl, and the field thus opened has since been successfully cultivated by many distinguished chemists. These investigations have led to the discovery of a number of metallic substitution derivatives of alcohol which are more or less closely allied to the compound ammonias. These bodies, however, are not all formed upon the type of ammonia. In some instances a single equivalent of the metal is combined with an equivalent of the alcohol radicle, whilst in others 2 equivalents of the alcohol radicle, in others 3 equivalents, and in some even 4 equivalents of the alcohol radicle, are combined with 1 equivalent of the metal.

The most probable explanation of the mode in which these compounds are formed, is that suggested by Frankland (*Phil. Trans.*, 1852, 440), who regards them as derivatives from the inorganic compounds of the various metals: and he considers that the number of equivalents of the alcohol radicles which combine with any given metal, is regulated by the proportion in which that metal tends to combine with the elements, hydrogen, sulphur, oxygen, &c. For example:—zinc forms compounds which correspond in composition to the oxide of zinc; and since zinc forms only a single oxide, the ethyl, and other alcohol derivatives of zinc, contain but a single equivalent of the alcohol radicle:—

Oxide of Zinc (ZnO). ;	Zinc-methyl	$Zn(C_2H_3)$
	Zinc-ethyl	$Zn(C_4H_5)$
	Zinc-amyl	$Zn(C_{10}H_{11})$

The tendency of arsenic is to the formation of compounds which contain 2, 3, or 5 equivalents of some other element, the bodies thus produced corresponding to realgar, to arseniuretted hydrogen, and to arsenic acid:—

Realgar ($As S_2$)	Kakodyl	As, $2 (C_2H_3)$
	Arseniodiethyl . .	As, $2 (C_4H_5)$
Arseniuretted Hydrogen (AsH_3)	Arseniotriethyl . .	As, $3 (C_4H_5)$
	Oxide of Kakodyl .	As, $[2 (C_2H_3) O]$
Arsenious Acid As $[O_3]$ . .	Chloride of Kakodyl	As, $[2 (C_2H_3) Cl]$
Arsenic Acid ($As O_5$) . . .	Hydrated Oxide of Arseniotetrethylium	As, $4 (C_4H_5) O, HO$
	Kakodylic Acid . .	As, $2 (C_2H_3) O_3, HO$
	Chloride of Arseniotetrethylium . .	As, $4 (C_4H_5), Cl.$

Antimony does not form any compound corresponding to realgar, but it yields bodies which contain 3 or 5 equivalents of some other element; and the alcohol compounds of this metal correspond to antimoniuretted hydrogen, and to antimonic acid:—

Antimoniuretted Hydrogen (H_3Sb)	Stibiotriethyl	$3 (C_4H_5) Sb$
Antimonic Acid (SbO_5) .	Oxide of Stibiotetrethylium	$4 (C_4H_5) Sb, O$
	Oxide of Stibiotriethyl .	$3 (C_4H_5) Sb, O_2$

Bismuth presents compounds which correspond to teroxide of bismuth:—

Oxide of Bismuth ($Bi O_3$)	Bistriethyl	Bi. $3 (C_4H_5)$
	Oxide of Bisethyl . .	Bi $[(C_4H_5) O_2]$

Mercury yields compounds corresponding in composition to the red oxide of the metal:—

Red Oxide of Mercury ($Hg_2 O_2$)	Oxide of Hydrargethyl	$Hg_2 [(C_4H_5) O]$

Lead yields a compound corresponding to plumbic acid, $2 PbO_2$:—

Peroxide of Lead $2(PbO_2) =$ (Pb_2O_4)	Oxide of Plumbethyl (hydrated) . . .	$Pb_2(C_4H_5)_2O, + xHO$

According to Löwig, other compounds of lead with ethyl also exist, but they have not yet been isolated in a state of purity. The formation of the compounds of tin is not so simply accounted for upon Frankland's view, since, according to Löwig, several polymeric forms, besides other compounds of these *organo-metallic* bodies may be obtained. Löwig has enumerated the following compounds of tin with ethyl:—

Stannethyl	$Sn (C_4H_5)$
Bistannethyl	$2 (Sn, C_4H_5)$
Quadristannethyl	$4 (Sn, C_4H_5)$
$\frac{4}{3}$ Stannethyl	$4 Sn, 3 (C_4H_5)$
$\frac{2}{3}$ Stannethyl	$2 Sn, 3 (C_4H_5)$
$\frac{4}{5}$ Stannethyl	$4 Sn, 5 (C_4H_5)$

Many of these compounds appear to have representatives in the methyl and in the amyl series. The formulæ of the more complex members must, however, be considered as still open to doubt.

The compounds of selenium and tellurium with the alcohol radicles, are closely allied to the class of bodies which we are now considering, although they present some analogy with the ethers, and they have already been alluded to (996) when speaking of these substances. The intermediate position occupied by selenium and tellurium between the metallic and non-metallic elements, explains why their compounds with the alcohol radicles should exhibit properties intermediate between those of the true ethers and these metallic derivatives of the alcohols. The tellurium and selenium ethers differ from the ordinary ethers in the tendency to combine with oxygen which they exhibit, thus forming bodies which unite with acids and yield definite salts. Tellurethyl $2\,(C_4H_5Te)$, for instance, becomes oxidized and forms the body, $2\,(C_4H_5)\,Te_2O_2$, and this compound, by its combination with oxalic acid, yields a crystalline salt, $2\,[\,(C_4H_5)_2Te_2O_2]\,C_4O_6,\ 2\,HO$.

Many of the compounds of the alcohol radicles with the metals, such for example as zinc-methyl, kakodyl, stibiotriethyl, and bistriethyl, have an affinity for oxygen so powerful that they take fire by simple contact with oxygen or with atmospheric air: but it is important to remark, that the results of such oxidation are very different in different cases. In some instances, when the operation is conducted slowly and with due care, *organo-metallic* oxides are procured, into the composition of which the alcohol radicle enters; they thus furnish bases which, like oxide of kakodyl, combine with acids, neutralizing them and forming well-defined crystallizable compounds. In other instances no such basic organo-metallic oxides can be obtained: thus zinc-methyl, and zinc-ethyl, although their affinity for oxygen is very intense, do not yield any organo-metallic base by the gradual action of oxygen upon them.

Kakodyl and arseniodiethyl (the kakodyl of the ethylic series), each unite with oxygen in two proportions: the lower oxide with one equivalent of oxygen in the case of kakodyl, exerting the properties of a powerful base, neutralizing acids, and forming with them crystallizable salts; whilst with three equivalents of oxygen a strong acid is produced; thus:—

Kakodyl	$As\ 2\,(C_2H_3)$.
Oxide of kakodyl .	$As\ 2\,(C_2H_3)\,O$.
Kakodylic acid . .	$HO,\ As\ 2\,(C_2H_3)\,O_3$.

Frankland accounts for the difference between the results of the oxidation of kakodyl and of zinc-methyl by saying, that in the case of oxide of zinc no binoxide is known, and as zinc-methyl is formed upon the type of oxide of zinc, there should therefore be no tendency to the formation of an oxide of zinc-methyl. In the case of kakodyl, the addition of an equivalent of oxygen produces a compound corresponding in a certain degree with arsenious acid :—

$$\text{As}\left.\begin{matrix}\text{O}\\\text{O}\\\text{O}\end{matrix}\right\}\text{Arsenious Acid,}\qquad \text{As}\left.\begin{matrix}\text{C}_2\text{H}_3\\\text{C}_2\text{H}_3\\\text{O}\end{matrix}\right\}\text{Oxide of Kakodyl ;}$$

whilst kakodylic acid corresponds to arsenic acid :—

$$\text{As}\left.\begin{matrix}\text{O}\\\text{O}\\\text{O}\\\text{O}\\\text{O}\end{matrix}\right\}\text{Arsenic Acid,}\qquad \text{As}\left.\begin{matrix}\text{C}_2\text{H}_3\\\text{C}_2\text{H}_3\\\text{O}\\\text{O}\\\text{O}\end{matrix}\right\}\text{Kakodylic Acid.}$$

This view is ingenious, and it may, as its author suggests, probably admit of further extension; Frankland has recently supported it by researches which seem to show that a basic organic radicle, such as methyl or ethyl, can be substituted for oxygen, which is strongly electro-positive. Thus he has obtained a *dinitroethylic acid* ($N_2C_4H_5O_3$), derived from 2 equivalents of deutoxide of nitrogen 2 (NO_2), in which 1 equivalent of oxygen has been displaced by ethyl; and the newly discovered *ethylotrithionic acid* [$S_3(C_4H_5)\ O_5$] may be regarded as formed from 3 equivalents of sulphurous acid 3 (SO_2), in which 1 equivalent of the oxygen has been displaced by ethyl. These bodies are produced by the action of zinc-ethyl upon deutoxide of nitrogen and sulphurous acid respectively (*Proceedings*, *Roy. Soc.* viii. 198). In order to illustrate the properties and mode of formation of these singular compounds, a description will now be given of a few of the organo-metallic bodies into the formation of which zinc, arsenic, and antimony enter.

(a) *Compounds of Zinc with the Alcohol Radicles.*

(1034) The properties of the compounds formed by zinc with the alcohol radicles are very remarkable, and these substances are further interesting in connexion with the process of isolating of the alcohol radicles themselves.

ZINC-METHYL (C_2H_3, Zn) is a very volatile, colourless, transparent, and highly mobile liquid, with a penetrating, peculiar, and insupportable odour. It is immediately decomposed by oxygen, chlorine, and iodine, forming compounds which are rather unstable. If placed in contact with atmospheric air, it takes fire instanta- [illegible] with a beautiful greenish-blue flame, and forming white clouds of oxide of zinc; in contact with pure oxygen it burns with explosion, and the presence of a small quantity of its vapour in combustible gases gives them the property of spontaneous inflammability on admixture with oxygen. When thrown into water, zinc methyl decomposes this liquid with explosive violence, attended with flame; and if the reaction be moderated, so as to prevent any intense elevation of temperature, the sole products of the decomposition are oxide of zinc and hydride of methyl (marsh gas); $C_2H_3, Zn + HO = C_2H_3, H + ZnO$.

Frankland suggests that, owing to the intense affinity of zinc methyl for oxygen and chlorine, it may be possible to employ it for effecting the substitution of methyl for oxygen and for chlorine, and it thus may throw some light upon the view of the constitution of the organo-metallic bodies which he has broached. In order to obtain zinc-methyl in a state of purity, iodide of methyl is sealed up, with an excess of dry granulated zinc, in a strong glass tube, drawn out to a capillary end, and exposed to a temperature of from 300° to 320° in an oil bath, until all the iodide of methyl has disappeared. A mass of white crystals, consisting of a compound of zinc-methyl with iodide of zinc, and a colourless, mobile liquid, which is zinc-methyl, is thus formed, and at the same time a considerable quantity of gaseous methyl is produced and confined. One portion of the iodide of methyl is converted into iodide of zinc and methyl,

$$2\ (C_2H_3I) + 2\ Zn = (C_2H_3, C_2H_3) + 2\ ZnI,$$

whilst another portion yields iodide of zinc and zinc-methyl,

$$C_2H_3I + ZnZn = C_2H_3Zn + ZnI.$$

The zinc-methyl may be obtained by breaking off the capillary extremity, and allowing the included gaseous methyl to escape, and the liquid contents are separated from the solid ones by distillation at a gentle heat in an atmosphere of dry hydrogen.

(1035) ZINC-ETHYL (C_4H_5, Zn = 2 vols. vapour). *Sp. gr. of vapour* 4·259; *of liquid* 1·182 at 64° F. (Frankland, *Phil. Trans.* 1855.)—This compound is a colourless, transparent, mobile liquid, which refracts light strongly, and is possessed of a peculiar powerful, but not disagreeable odour. It is not solidified by a cold of —8° F. It boils at 244°, and may be distilled without change in vessels filled with carbonic acid, or with hydrogen. Zinc-ethyl is less inflammable than zinc-methyl, but its affinity for oxygen is sufficiently intense to cause it to take fire as soon as the liquid is brought into contact with that gas, or with atmospheric air, when it burns with a brilliant blue flame, fringed with green, and forms dense white clouds of oxide of zinc. If a cold piece of glass, or of porcelain, be held in the flame, it becomes coated with a deposit of metallic zinc, surrounded by a white ring of the oxide of this metal. If the oxidation be allowed to take place more slowly, zinc-alcohol C_4H_5, ZnO (or ethylate of zinc) is the principal product; and this mode of the formation of zinc-alcohol from the direct combination of zinc-ethyl with oxygen, is certainly very remarkable. Water immediately decomposes zinc-ethyl; oxide of zinc, and the gaseous hydride of ethyl (C_4H_5, H) being the result:

$$C_4H_5, Zn + HO = C_4H_5, H + ZnO.$$

Iodine, bromine, and chlorine, decompose zinc-ethyl with great violence; if the action be moderated, iodide, bromide, or chloride of zinc is formed, whilst the corresponding compound of ethyl with the halogen is formed; in the case of iodine, the reaction may be thus represented:—

$$C_4H_5, Zn + 2 I = C_4H_5I + ZnI.$$

A similar effect is produced if zinc-ethyl be heated with powdered sulphur, the double sulphide of zinc and ethyl being formed.

Preparation.—Zinc-ethyl is obtained by heating anhydrous iodide of ethyl, diluted with an equal volume of anhydrous ether[*] (to regulate the reaction) with twice its weight of well-dried granulated zinc. The mixture is introduced into a sealed glass tube, and heated in a digester to about 266° F. for twelve or eighteen hours. When large quantities are required, the safest plan is to conduct the operation in a strong metallic vessel, of particular construction. A full description of this apparatus is given by Frankland in his paper. If the materials employed for the preparation of the zinc-ethyl were really anhydrous, very little permanent gas is produced, but if moisture be present, a quantity of hydride of ethyl is formed. After the apparatus has become cool, the permanent gas, if any, is allowed to escape; and the zinc-ethyl is distilled from the materials employed in its preparation, in vessels filled with carbonic acid or hydrogen. Particular modes of manipulation are required during the distillation and purification of the product, in order to prevent the access of air, which would oxidize and destroy the compound. For details upon these points, the reader is referred to the memoir already cited.

(1036) *Zinc-amyl* ($C_{10}H_{11}, Zn$).—This body is obtained by decomposing iodide of amyl in a sealed tube, at a temperature of 356°. It forms a colourless, transparent liquid, which emits fumes, and rapidly absorbs oxygen when exposed to the air; but it does not take fire spontaneously. Water decomposes it into oxide of zinc and hydride of amyl:—

---

[*] This mixture, to deprive it completely of moisture, is agitated with about one-twentieth of its weight of anhydrous phosphoric acid.

$$C_{10}H_{11}, Zn + HO = C_{10}H_{11}, H + ZnO.$$

(*b*) *Compounds of the Alcohol Radicles with Arsenic.*

Arsenic forms with the alcohol radicles three classes of compounds, which have hitherto been examined only in the methyl and in the ethyl series:—

1. Arseniodimethyl or kakodyl	$C_4H_6\,As = 2(C_2H_3)As$	Arseniodiethyl (ethylic kakodyl)	$C^8\,H_{10}As = 2(C_4H_5)As$
2. Arseniotrimethyl	$C_6H_9\,As = 3(C_2H_3)As$	Arseniotriethyl .	$C_{12}H_{15}As = 3(C_4H_5)As$
3. Oxide of Arseniotetramethylium . . .	$C_8H_{12}As_2O = 4(C_2H_3)As_2O$	Oxide of Arseniotetrethylium .	$C_{16}H_{20}As_2O = 4(C_4H_5)As_2O$

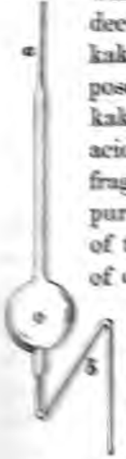
(1037) KAKODYL; *Arseniodimethyl* ($2\,C_2H_3, As = C_4H_6As$); *Sp. gr. of vapour* 7·1.—This is an extremely poisonous, colourless, viscous liquid, heavier than water; it emits fumes, and takes fire spontaneously when exposed to the air. Its vapours have a disgusting arsenical odour. The boiling point of kakodyl is about 338°; at 21° it becomes solid and crystallizes in square prisms. It is only slightly soluble in water, but is readily dissolved by alcohol and by ether. When heated to about 750° it is entirely decomposed into metallic arsenic and a gaseous mixture consisting of 2 volumes of marsh gas and 1 volume of olefiant gas:—

$$2\,(\overbrace{C_4H_6\,As}^{\text{Kakodyl.}}) = As_2 + 2\,(\overbrace{C_2H_4}^{\text{Marsh Gas.}}) + \overbrace{C_4H_4}^{\text{Olefiant Gas.}}.$$

Kakodyl burns in oxygen with a pale blue flame, producing water, with carbonic and arsenious acids: but if atmospheric air be admitted bubble by bubble into kakodyl, white fumes are formed, and oxide of kakodyl $(C_4H_6As)O$ is the result: an excess of oxygen converts it into kakodylic acid $(C_4H_6As)O_3$; but if the supply of oxygen be insufficient to complete this change, kakodylate of kakodyl $(C_4H_6As)O, (C_4H_6As)O_3$ (binoxide of kakodyl) is produced.

The remarkable peculiarity of kakodyl is its power of thus uniting directly with oxygen; and it exhibits a similar tendency to combine with sulphur, chlorine, &c.; in this manner it performs the part of a simple metallic body, since the group C_4H_6As (which may be represented by the abbreviated symbol Kd), admits of being substituted for hydrogen. The discovery of kakodyl was an important step in the development of the theory of mistry, as it furnished the first instance of the isol organic metallic basyl: although other bodies more o gous to it in this respect are now known.

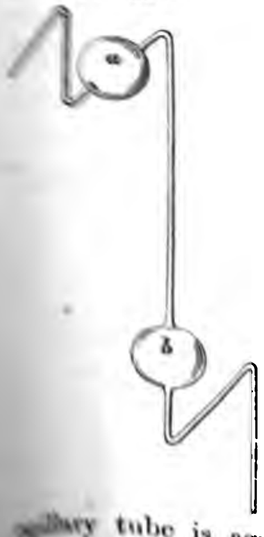
Fig. 335.



Kakodyl was obtained by Bunsen from which, when treated with fragments of granul decomposed; chloride of zinc being formed. kakodyl is liberated. The chloride employed pose must be perfectly anhydrous, and free f kakodyl. After digestion with concentrated acid, the chloride is allowed to stand for sever fragments of quicklime and chloride of cal purification of the chloride must be effected in of the form shown in fig. 335, the quicklime of calcium being first introduced into the bul

In order to avoid the contact of purified material, a current of dry carboni admitted by the fine tube *a*, in order to atmospheric air completely, and the capill then sealed: when the chloride of kak introduced, the point of the capillary tub and by means of a caoutchouc tube it is connected syringe: the tube *b* is then open to dip into the liquid chloride, movement of the piston is dr bulb. The decomposition mus in an apparatus similar to that 336. The zinc having first been bulb *a*, the apparatus is to be fi bonic acid, and a portion of th kakodyl is admitted. The capil then sealed, and heat is applied which acts as a retort, *b* servi ceiver. The zinc gradually beco without any evolution of gas; w has ceased, the apparatus is al and the capillary tube at *a* is boiled water: the bulb is then to expel a portion of the carb water enters as the apparatus pillary tube is again sealed: the water acting u ised mass in the bulb *a*, dissolves the chlo

Fig. 336.



and liberates kakodyl in the form of an oily fluid, which is transferred to a bulb-tube of the form of fig. 335, the bulb having been filled with chloride of calcium, and the air displaced by means of carbonic acid, in the manner already described: here it is dried, then transferred to the bulb apparatus (fig. 336), and rectified from a fresh portion of zinc. Kakodyl may also be obtained by the action of mercury upon sulphide of kakodyl.

(1038) *Compounds derived from Kakodyl.*—Bunsen has described a large number of compounds of kakodyl; some of the more important are the following:—

Kakodyl	(C_4H_6As)
Oxide of kakodyl	$(C_4H_6As)\ O$
Binoxide of kakodyl (kakodylate of kakodyl)	$(C_4H_6As)\ O,\ (C_4H_6As)\ O_3$
Sulphate of kakodyl	$(C_4H_6As)\ O,\ SO_3$
Kakodylic acid	$HO,(C_4H_6As)\ O_3$
Kakodylate of silver	$AgO,\ (C_4H_6As)\ O_3$
Protosulphide of kakodyl . . .	$(C_4H_6As)\ S$
Bisulphide of kakodyl	$(C_4H_6As)\ S,\ (C_4H_6As)\ S_3$
Tersulphide of kakodyl (sulphokakodylic acid)	$(C_4H_6As)\ S_3$
Sulphokakodylate of silver . . .	$AgS,\ (C_4H_6As)\ S_3$
Protochloride of kakodyl . . .	$(C_4H_6As)\ Cl$
Terchloride of kakodyl	$(C_4H_6As)\ Cl_3$
Oxychloride of kakodyl . . .	$(C_4H_6As)\ O,\ 3(C_4H_6As,\ Cl)$
Hydrargo-oxychloride of kakodyl	$(C_4H_6As)\ O,\ HgCl$

Oxide of Kakodyl ($C_4H_6As,\ O$); *Sp. gr. of vapour* 7·55.—The preparation of the compounds of kakodyl, owing to the inflammability of many of them, and their highly poisonous character, is both difficult and dangerous. Oxide of kakodyl constitutes in an impure form the horribly fœtid, spontaneously inflammable liquid, formerly known as *Cadet's fuming liquor*, or *alkarsin*, which is obtained by the distillation of a mixture of equal parts of dried acetate of potash and arsenious acid. The receiver must be fitted to the neck of the retort, and furnished with a tube for carrying off the gaseous products into the chimney; the retort is then to be heated by a sand bath, the temperature of which is gradually raised to dull redness. The distilled liquid separates into three layers; the lower one consists of arsenic; above this is a brown oily liquid, consisting chiefly of a mixture of impure kakodyl and oxide of kakodyl; and above this is a mixture of water, acetone, and acetic acid. A copious disengagement of carbonic acid and of marsh gas accompanies the operation. The stratum of alkarsin (oxide of kakodyl) is drawn off, by means of a syphon filled with boiled water, into a flask also filled with the same liquid, into which the longer limb of the syphon is plunged with a view of preventing the contact of the air with the inflammable alkarsin. It is washed with boiled water, and then rectified from hydrate of potash in a current of hydrogen: air is then gradually admitted to the distillate, sufficiently slowly to prevent it from taking fire. The liquid thus obtained consists of a mixture of the oxide of kakodyl and kakodylic acid; it is dissolved in water and distilled. At first a quantity of water having the odour of kakodyl passes over, and when the temperature rises to 248°, the oily liquid which distils is nearly pure oxide of kakodyl. A second rectification from caustic baryta in vessels from which air is excluded, furnishes the compound in a state of purity. All these operations must be conducted with the greatest possible care, and with the adoption of special precautions, on account of the deadly nature of the vapours. Full particulars upon all these points are given by M. Bunsen in the interesting and remarkable series of memoirs which he has published upon the compounds of kakodyl and its derivatives. These papers are worthy of careful study as models of ingenuity and precision in the prosecution of a research beset with unusual difficulty and danger (Liebig's *Annal.*, xxxvii. 1; xlii. 14; and xlvi. 1). Oxide of kakodyl is a colourless, limpid, ethereal liquid, endowed with a penetrating odour, and boiling at about 248°; it is insoluble in water, but soluble in alcohol. It slowly absorbs oxygen from the air, and combines with acids to form salts: the sulphate crystallizes in radiated needles.

Oxide of kakodyl also combines with the electro-negative chlorides with facility. If an alcoholic solution of corrosive sublimate be mixed with a dilute solution of Cadet's liquor in alcohol, an abundant white precipitate is formed, and the intolerable odour of kakodyl disappears completely. The precipitate if collected, pressed to remove the adhering mother liquor, and redissolved in boiling water, is deposited in well defined crystals ($C_4H_6AsO, HgCl$). The ready formation of this crystalline compound offers one of the best means of purifying the crude compounds of kakodyl. When this mercurial compound is distilled with concentrated hydrochloric acid it furnishes *chloride of kakodyl* ($(C_4H_6As)Cl$), in the form of a colourless liquid, which boils at about 212°, and is not frozen by a cold of —49°. It takes fire spontaneously in the air, and in an atmosphere of chlorine; in the latter case depositing carbon abundantly. Its vapour is still more deleterious than that of the oxide: chloride of kakodyl is insoluble in water and in ether, but very soluble in alcohol. *Iodide* and *bromide of kakodyl* may be obtained by treating the mercurial compound with hydriodic or with hydrobromic acid.

The *cyanide of kakodyl* (C_4H_6As, C_2N; or KdCy) shows a remarkable tendency to crystallization; it appears to be the most deadly compound of the whole series, a single grain diffused in vapour through a room being sufficient to produce numbness of the hands and feet, vertigo, and even syncope in those exposed to its effects. It may be obtained in brilliant prisms which fuse at 91°, and boil at about 284°, by decomposing a concentrated solution of cyanide of mercury with oxide of kakodyl, and rectifying the crystals over caustic baryta. The vapour of cyanide of kakodyl has a density of 4·63.

Sulphur combines with kakodyl in three proportions; the *protosulphide of kakodyl* (KdS) is a colourless, very fœtid liquid, which absorbs oxygen rapidly from the air. Its boiling point is above 212°, and it emits a vapour of sp. gr. 7·72. It is readily soluble in alcohol and in ether: it combines easily with an additional quantity of sulphur, and becomes converted into the solid *bisulphide* (KdS_2). The *tersulphide* (KdS_3) possesses the properties of a sulphur acid. If an alcoholic solution of the protosulphide be mixed with an alcoholic solution of nitrate of copper, octohedral crystals of adamantine lustre are deposited; they are permanent in the air, and consist of a double sulphide of kakodyl and copper (C_4H_6AsS, CuS). The protosulphide of kakodyl may be obtained by distilling Cadet's liquor with sulphide of barium.

Kakodylic acid (HO, C_4H_6As, O_3) crystallizes in oblique equilateral prisms which are soluble in water and in alcohol. It is remarkable that it appears to possess little or no poisonous action upon the animal system, seven grains of it having been injected into the blood of a rabbit without producing any marked effect. It is a weak acid, and decomposes the carbonates slowly. Its salts, with the exception of the silver salt, crystallize with difficulty. The acid is easily obtained by treating oxide of kakodyl with red oxide of mercury: metallic mercury is reduced whilst the acid is dissolved.

(1039) *Arseniodiethyl* ($C_8H_{10}As = 2\ (C_4H_5)As$) forms a series of compounds parallel to those of kakodyl, but it does not so instantaneously burst into flame on exposure to air, and, generally, its affinities are somewhat less powerful.

(1040) *Arseniotrimethyl* $3(C_2H_3)As$, corresponds in composition with the analogous compound of the ethyl series, which has been more completely examined.

Arseniotriethyl $[C_{12}H_{15}As = 3(C_4H_5)As]$; *Sp. gr. of liquid* 1·151, *of vapour* 5·278.—This is a fuming, colourless, mobile liquid, of high refracting power, with the oppressive odour of arseniuretted hydrogen. It is miscible with alcohol and ether, but not with water. It begins to boil at 284°; but it undergoes partial decomposition during distillation. It does not usually take fire by exposure to the air unless gently heated, though it rapidly absorbs oxygen. It also becomes gradually oxidized if its solution in ether be exposed to the air; and it then produces a base, $3(C_4H_5)AsO_2$, which requires two equivalents of acid for its saturation. A sulphide, chloride, and iodide may be obtained, each of which contains two equivalents of the electro-negative body to one of arseniotriethyl; the iodide having the formula, $3(C_4H_5)As, I_2$. Arseniotriethyl is obtained by the action of iodide of ethyl upon an alloy of arsenic and sodium; under these circumstances it is accompanied by arseniodiethyl, from which it is separated by distillation; the latter compound being the less volatile, remains in the retort. These operations must be performed in vessels filled with carbonic acid gas. The compounds of arseniotriethyl have the closest analogy with those of stibiotriethyl (1043).

(1041) *Oxide of Arseniotetrethylium*, $4(C_4H_5As)O$.—If arseniotriethyl be treated with iodide of ethyl, it combines with it and forms a new compound, which has been termed iodide of arseniotetrethylium $[4(C_4H_5)As, I]$. It may be crystallized from water or from alcohol, and when its aqueous solution is treated with oxide of silver, iodide of silver is formed, while the oxide of arseniotetrethylium is obtained in solution. It may be procured in the form of a white hydrated solid by evaporation *in vacuo*, and like the ordinary ammonium bases, it presents the properties of a powerful and caustic alkali. It forms crystallizable salts, which when neutral contain 1 equivalent of acid.

By treating kakodyl with iodide of ethyl, an *iodide of arseniomethylethylium* $[2(C_4H_5)\ 2(C_2H_3)\ I]$ is formed; from which the oxide $[2(C_4H_5)\ 2(C_2H_3)I, O]$ may be obtained by the action of oxide of silver. A corresponding compound containing amyl $[2(C_{10}H_{11})\ 2(C_2H_3)I]$ may be obtained by substituting iodide of amyl for iodide of ethyl when acting upon kakodyl. The attempts to isolate the unoxidized compound metals of the form of arseniotetrethylium $[4(C_4H_5)As]$ have as yet been fruit

(*c*) *Compounds of Antimony with the Alcohol Radicles.*

(1042) The alcohol derivatives of antimony have been carefully examined by Löwig and Schweizer (Liebig's *Annalen*, lxxv. 315), and by Landolt, (*Ib.* lxxviii. 91, and lxxxiv. 44). No compounds of antimony corresponding to the kakodyl series have been discovered; but those analogous to the second and third class of the arsenical compounds have been studied. The following are the principal compounds with methyl and with ethyl which correspond to the second series of the arsenical compounds:—

Stibiotrimethyl . . .	$C_6 H_9 Sb$	$= 3 (C_2H_3)Sb$
Oxide of stibiotrimethyl	$C_6 H_9 Sb, O_2$	$= 3 (C_2H_3)Sb, O_2$
Sulphide "	$C_6 H_9 Sb. S_2$	$= 3 (C_2H_3)Sb, S_2$
Chloride "	$C_6 H_9 Sb, Cl_2$	$= 3 (C_2H_3)Sb, Cl_2$
Sulphate "	$C_6 H_9 Sb, O_2. 2 SO_3$	$= 3 (C_2H_3)Sb, O_2, 2 SO_3$
Nitrate "	$C_6 H_9 Sb, O_2. 2 NO_5$	$= 3 (C_2H_3)Sb, O_2, 2 NO_5$

Stibiotriethyl	$C_{12}H_{15}Sb$	$= 3 (C_4H_5)Sb$
Oxide of stibiotriethyl .	$C_{12}H_{15}Sb, O_2$	$= 3 (C_4H_5)Sb, O_2$
Sulphide "	$C_{12}H_{15}Sb, S_2$	$= 3 (C_4H_5)Sb, S_2$
Chloride "	$C_{12}H_{15}Sb, Cl_2$	$= 3 (C_4H_5)Sb, Cl_2$
Sulphate "	$C_{12}H_{15}Sb, O_2. 2 SO_3$	$= 3 (C_4H_5)Sb, O_2, 2 SO_3$
Nitrate "	$C_{12}H_{15}Sb, O_2. 2 NO_5$	$= 3 (C_4H_5)Sb, O_2, 2 NO_5$

The radicles stibiotrimethyl and stibiotriethyl at the first glance seem to resemble ammonia in composition, since they correspond to antimoniuretted hydrogen in which the three equivalents of hydrogen have been displaced by methyl or by ethyl, but they entirely differ from ammonia in their mode of combination; they each form an oxide with two equivalents of oxygen;* and this oxide requires two equivalents of hydrochloric or of nitric acid for its saturation. Frankland views stibiotriethyl as the representative of the oxide of antimony (SbO_3), in which the three equivalents of oxygen have been displaced by an equal number of equivalents of ethyl; oxide of stibiotriethyl representing antimonic acid ($SbO_3. O_2$). A similar explanation may be applied to the corresponding compounds of arsenic, arseniotriethyl and its oxide.

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* Merck considers that he has proved that the oxide of stibiotriethyl is monobasic, and contains only 1 equivalent of oxygen, and that the iodide of Löwig and Schweizer is $3 (C_4H_5) SbI, HI$, and not a biniodide, from which it differs by containing 1 equivalent more of hydrogen: and he has obtained a substance in brilliant octohedral crystals, which he represents as $3 (C_4H_5) Sb, I$, by acting upon Löwig's biniodide, with ammonia. It is not impossible, however, that Merck's compound is an oxyiodide [$3 (C_4H_5)Sb,O,I$]; in which case the differences between its discoverer, and Löwig and Schweizer, would all be accounted for; but the subject requires further investigation.

Antimony also forms a second class of organo-metallic compounds, the methyl series of which is represented as follows:—

Oxide of Stibiotetramethylium	$C_8H_{12}SbO$	$=$	$4\ (C_2H_3)\ Sb,\ O$
Sulphide ,,	$C_8H_{12}SbS$	$=$	$4\ (C_2H_3)\ Sb,\ S$
Chloride ,,	$C_8H_{12}SbCl.$	$=$	$4\ (C_2H_3)\ Sb,\ Cl$
Sulphate ,,			$4\ (C_2H_3)\ Sb,\ O.\ SO_3$
Bisulphate ,,			$4\ (C_2H_3)\ Sb,\ O.\ HO.\ 2\ SO_3$
Nitrate ,,			$4\ (C_2H_3)\ Sb,\ O.\ NO_5.$

This group appears to correspond exactly with the ammonium series, with which indeed it presents the most striking analogies. Still it admits of being regarded from Frankland's point of view, in which case its oxide would be regarded as a compound corresponding to antimonic acid, in which the places of 4 out of the 5 equivalents of oxygen are occupied by an equal number of equivalents of methyl; thus,

$$\overbrace{(SbO_4.\ O)}^{\text{Antimonic Acid.}} \quad ; \quad \overbrace{(Sb\ 4\ (C_2H_3).\ O)}^{\text{Oxide of Stibiotetramethylium.}} \quad ;$$

this new oxide requires only 1 equivalent of an acid for its saturation. In connexion with this view it is worthy of remark that neither stibiotetramethylium $[4\ (C_2H_3)Sb]$ nor its anhydrous oxide has hitherto been isolated; and in the nitrogen series, both ammonium and oxide of ammonium are unknown in a separate form.

These speculations upon molecular arrangement must, however, await the result of further experiment, before any decided opinion can be formed upon their merits.

(1043) STIBETHYL, or *Stibiotriethyl* $[3\ (C_4H_5)Sb]$; *Sp. gr. of liquid*, 1·324, *of vapour* 7·438.—In order to procure stibiotriethyl, an alloy of antimony with potassium must be prepared by heating a mixture of 4 parts of powdered antimony and 5 of crude tartar in a covered crucible. This alloy, after being reduced to powder, is to be mixed with three times its weight of siliceous sand and placed in a retort with iodide of ethyl. The operation must be conducted upon small quantities at a time, and in an atmosphere of carbonic acid: it requires a number of minute precautions (Löwig and Schweizer, *loc. cit.*). Stibiotriethyl is a heavy, limpid liquid, with an insupportable odour of onions. It is insoluble in water, but very soluble in alcohol and in ether. When a glass rod is dipped into pure stibiotriethyl and exposed to the air, the liquid emits dense white fumes, and takes fire in a few seconds, burning with a white luminous flame. It boils at 317°.

Stibiotriethyl decomposes concentrated hydrochloric acid; hydrogen being liberated, whilst bichloride of stibiotriethyl is [illegible] as a heavy, insoluble oil.

The *binoxide* is obtained by acting on stibiotriethyl with red oxide of mercury. It forms a viscous transparent liquid, soluble in water and in alcohol. The solution has a very bitter taste, but it does not appear to be poisonous. It is not volatile, and forms salts which crystallize with difficulty, except the nitrate, which forms beautiful rhomboidal, readily soluble crystals, which melt at 144° into a colourless liquid, and are decomposed with deflagration on raising the heat.

Bisulphide of Stibiotriethyl [$3\,(C_4H_5)\,Sb, S_2$].—If stibiotriethyl and sulphur be mixed under water, they enter directly into combination, and great heat is evolved during the reaction: the compound is soluble in water, and may be obtained in crystals on evaporation. This solution when mixed with solutions of the metallic salts precipitates the metallic sulphides, (just as sulphide of potassium would do,) while a salt of oxide of stibiotriethyl remains dissolved:—for instance, if sulphate of copper be mixed with a solution of sulphide of stibiotriethyl, sulphate of stibiotriethyl and sulphide of copper are formed:—

$$3\,(C_4H_5)\,Sb, S_2 \;+\; 2\,(CuO, SO_3) \;=\; 2\,(CuS) \;+\; 3\,(C_4H_5)\,SbO_2, 2\,SO_3.$$

Biniodide of Stibiotriethyl is soluble in alcohol, from which it crystallizes in long transparent colourless needles. It is also soluble in ether and in hot water.

Stibiotrimethyl [$3(C_2H_3)Sb$] may be formed in a manner similar to that directed for stibiotriethyl, which in properties it greatly resembles.

(1044) *Oxide of Stibiotetramethylium* ($C_8H_{12}SbO = 4\,(C_2H_3)\,Sb, O$).—When stibiotrimethyl is brought into contact with iodide of methyl, the two bodies combine, and a crystalline iodide of stibiotetramethylium is the result:

$$\overbrace{3\,(C_2H_3)\,Sb}^{\text{Stibiotrimethyl.}} \;+\; \overbrace{C_2H_3I}^{\text{Iodide of Methyl.}} \;=\; \overbrace{4\,(C_2H_3)Sb, I.}^{\text{Iodide of Stibiotetramethylium.}}$$

This compound is soluble in boiling water and in alcohol, from either of which solutions it may be obtained in crystals. When treated with oxide of silver, the oxide of stibiotetramethylium is separated, whilst iodide of silver is formed. This oxide is freely soluble in water and in alcohol. Its solution is very caustic and absorbs carbonic acid from the air, presenting most of the usual characters of an ammonium base, and precipitating many of the metallic oxides from their salts. Upon evaporating its aqueous solution *in vacuo*, the oxide may be obtained in crystals, which if heated with due care in a tube, may be volatilized without undergoing decomposition.

Its salts are very stable and are readily soluble; they have a bitter taste, but are not poisonous: they present great similarity in appearance to those of potash and ammonia. On the addition of soda or potash to their solutions, the oxide of stibiotetramethylium is liberated.

CHAPTER IV.

AMIDES, AND ORGANIC BASES.

§ I. AMIDES AND THEIR VARIETIES.

(1045) *Amides.*—It has been already stated (312), that under certain circumstances a portion of the hydrogen of ammonia may be displaced by potassium, and a compound is thus formed consisting of KH_2N, which has been termed *amide* of potassium. When oxalate of ammonia is submitted to distillation, a white sublimate is obtained (507, *note*), in which the elements of oxalate of ammonia, minus 2 equivalents of water, are present; to this sublimate Dumas, by whom it was discovered, gave the name of *oxamide.* The following equation represents the relation which exists between oxamide and oxalate of ammonia:—

$$\overbrace{H_4NO,\ C_2O_3}^{\text{Oxalate of Ammonia.}} = \overbrace{H_2NC_2O_2}^{\text{Oxamide.}} + 2\,HO;$$

or if the oxalic be regarded as a dibasic acid:—

$$2\,(H_4N,\ O)\ C_4O_6 = 2\,(H_2N)\ C_4O_4 + 4\,HO.$$

Now it is found that other salts of ammonia, when submitted to dry distillation, or otherwise deprived of water, yield compounds analogous to oxamide. When the ammonia salts of the monobasic acids lose 2 equivalents of water, or when the neutral ammonia salts of the dibasic acids lose 4 equivalents of water, the resulting compounds are called *amides;* those obtained from the dibasic acids being further distinguished as *diamides.* It has been proposed to account for the formation of these compounds by the hypothesis, that they contain a certain hydride of nitrogen, which has not hitherto been procured in a separate form, but to which the composition H_2N, and the name of *amidogen* (312) has been assigned.

(1046) *Nitriles.*—But the amides themselves also admit of being deprived of water: and when the amide of a monobasic acid has thus been made to lose two additional equivalents of water, it yields a compound belonging to a class known under the generic term of *nitriles*. Acetamide, less two equivalents of water, yields aceto-nitrile:—

$$\overbrace{H_2N, C_4H_3O_2}^{\text{Acetamide.}} \quad = \quad 2\,HO \quad + \quad \overbrace{HN, C_4H_2}^{\text{Aceto-nitrile.}};$$

and, in like manner, oxamide gives oxalo-nitrile;—

$$\overbrace{2(H_2N)\,C_4O_4}^{\text{Oxamide.}} \quad = \quad 4\,HO \quad + \quad \overbrace{2(NC_2)}^{\text{Oxalo-nitrile.}}.$$

It is worthy of remark, that oxalonitrile has the same composition as cyanogen, and is not only metameric, but also identical with it; so that cyanogen admits of being regarded as the nitrile of oxalic acid; and thus a certain analogy may be traced between cyanogen and the products obtained by the dehydration of the ammonia salts; the nitriles of the fatty acids $HO, (C_nH_{n-1}), O_3$, being in fact identical with the hydrocyanic ethers (997). These nitriles, when fused with potassium, yield cyanide of potassium and disengage hydrogen, mixed with gaseous hydrocarbons. The nitriles, when treated with an alkali, do not reproduce hydrocyanic acid, and their corresponding alcohol; but they recombine with the elements of water, and form ammonia, and a salt of the original acid from which the nitrile was obtained. Thus, benzonitrile when boiled with a solution of potash, yields benzoate of potash and ammonia:—

$$\overbrace{C_{14}H_5N}^{\text{Benzonitrile.}} + KO, HO + 2\,HO = \overbrace{KO, C_{14}H_5O_3}^{\text{Benzoate of Potash.}} + H_3N.$$

The nitriles may also be obtained from the corresponding ammoniacal salts, by the action of an excess of anhydrous phosphoric acid:—in this way benzoate of ammonia may be converted into benzonitrile, since the latter contains the elements of benzoate of ammonia deprived of 4 equivalents of water; the hydrogen being supplied from the elements of the ammonia, whilst the oxygen is derived mainly from those of the acid:—

$$\overbrace{H_4NO, C_{14}H_5O_3}^{\text{Benzoate of Ammonia.}} \quad = \quad 4\,HO \quad + \quad \overbrace{C_{14}H_5N}^{\text{Benzonitrile.}}.$$

None of the nitriles hitherto procured contain oxygen, since all the salts which at present are known to yield them are formed either from monobasic acids of the form $(HO, C_xH_yO_3)$, or from dibasic acids of the form $(2\,HO, C_xH_yO_6)$.

The relations subsisting between benzoate of ammonia, benzamide, and benzonitrile, will exhibit the nature of the connexion between the ammonia salt, the amide, and the nitrile of a monobasic acid :—

$$\overbrace{H_4NO,\ C_{14}H_5O_3}^{\text{Benzoate of Ammonia.}} - 2\,HO = \overbrace{H_2NC_{14}H_5O_2}^{\text{Benzamide.}}\ (\text{or } C_{14}H_7NO_2);$$

$$\text{and } \overbrace{H_2NC_{14}H_5O_2}^{\text{Benzamide.}} - 2\,HO = \overbrace{C_{14}H_5N}^{\text{Benzonitrile.}}.$$

(1047) *Amidated Acids.*—If, instead of operating upon a *neutral* salt of ammonia, obtained from either a monobasic or a dibasic acid, any of the *acid* salts formed by ammonia with the dibasic acids be subjected to dehydration, a body is produced belonging to the class of *amidic*, or *amidated acids*. M. Balard in distilling binoxalate of ammonia thus obtained an azotised acid, which has been termed oxamic acid :—

$$\overbrace{H_4NO,\ HO,\ C_4O_6}^{\text{Acid Oxalate of Ammonia.}} = 2\,HO + \overbrace{HO,\ H_2N,\ C_4O_5}^{\text{Oxamic Acid.}}.$$

This substance may serve as the type of a numerous class of compound acids, formed in a similar manner. The ammonia loses hydrogen, and the portion of the acid attached to the ammonia of the original salt loses oxygen, whilst that portion of acid which was attached to water as a base remains unaltered; so that oxamic acid may be viewed as a compound of unchanged oxalic acid and of oxamide :—

$$\overbrace{2\,(HO,\ H_2N,\ C_4O_5)}^{\text{Oxamic acid.}} = \overbrace{2\,(H_2N)C_4O_4}^{\text{Oxamide.}} + \overbrace{2\,HO,\ C_4O_6}^{\text{Oxalic acid.}}.$$

The amidated acids may also be obtained by acting upon the anhydride of a dibasic acid (1101) with dry ammonia in excess: the two bodies combine together, but the compound which is produced is found on examination to give evidence of the presence of but one half of the ammonia in the form of an ordinary ammoniacal salt; the second half having united with the elements of the acid to produce a new compound acid, which is the amidated acid of the one originally employed (Laurent). Thus, 1 equivalent of anhydrous camphoric acid when acted upon by 1 equivalent of ammonia, yields 1 equivalent of hydrated camphoramic acid; the decomposition being supposed to consist in the conversion of one-half of the acid into camphoramide, while an equivalent of water is given off and enters into combination with the other half of the acid; these two bodies, camphoramide and hydrated camphoric acid then unite and form the new acid :—

$$\overbrace{C_{20}H_{14}O_6}^{\text{1 eq. of Camphoric Anhydride.}} + H_3N = \underbrace{\overbrace{HO,\ C_{10}H_7O_3}^{\text{½ eq. of Hydrated Camphoric acid.}} + \overbrace{H_2N,\ C_{10}H_7O_2}^{\text{½ eq. of Camphoramide.}}}_{\text{1 eq. of Hydrated Camphoramic Acid.}}$$

This amidated acid may be converted into camphoramate of ammonia by causing it to unite with a second equivalent of ammonia.

The amidated acids may therefore be viewed as monobasic compounds derived from dibasic acids, in which one half of the group composing the original dibasic acid, is displaced by one half of the group which forms the amide of the acid; the combination of 1 equivalent of the original dibasic acid with 1 of the amide furnishing 2 equivalents of the monobasic amidated acid. To take again the case of the camphoric acid :—

$$2\,\overbrace{\mathrm{HO,\ C_{20}H_{14}O_6}}^{\text{Hydrated Camphoric Acid.}} + \overbrace{\mathrm{(H_2N)_2C_{20}H_{14}O_4}}^{\text{Camphoramide.}} = 2\,\overbrace{\mathrm{(HO,\ H_2N,\ C_{20}H_{14}O_5)}}^{\text{Hydrated Camphoramic Acid.}}.$$

When the aqueous solutions of the amidated acids are boiled, they quickly assimilate the elements of water, and become reconverted into acid salts of ammonia.

(1048) *Imides.*—Intermediate between the amides and the nitriles there is a third class of bodies, the ***imides***, which contain nitrogen, and in which, if we are consistent, the existence of a body termed *imidogen* HN, (or ammonia, less two equivalents of hydrogen,) must be assumed to exist. These compounds are not numerous, but several of them are well known. They are obtained by a process of dehydration from certain acid salts of ammonia, and from the amidated acids procurable from these salts; succinic, camphoric, and phthalic acids, for instance, each yield imidated compounds. The relation of these bodies to their respective acids will be seen by the following comparison :—

Hydrated camphoric acid	$2\ \mathrm{HO,\ C_{20}H_{14}O_6}$
Acid camphorate of ammonia	$\mathrm{HO,\ H_4NO,\ C_{20}H_{14}O_6}$
Camphoramic acid (amidated camphoric acid)	$\mathrm{HO,\ H_2N,\ C_{20}H_{14}O_5}$
Camphorimide	$\mathrm{HN,\ C_{20}H_{14}O_4}$

Phthalic acid	$2\ \mathrm{HO,\ C_{16}H_4O_6}$
Acid phthalate of ammonia	$\mathrm{HO,\ H_4NO,\ C_{16}H_4O_6}$
Phthalamic acid (amidated phthalic acid) .	$\mathrm{HO,\ H_2N,\ C_{16}H_4O_5}$
Phthalimide	$\mathrm{HN,\ C_{16}H_4O_4}$.

Hence it will be perceived, that the imides are bodies formed from the amidated acids by depriving these compounds of two equivalents of water, just as the amidated acids are themselves obtained from the acid salts of ammonia by depriving the latter of two equivalents of water :—

$$\overbrace{\mathrm{HO,\ H_4NO,\ C_{20}H_{14}O_6}}^{\text{Acid Camphorate of Ammonia.}} = 2\,\mathrm{HO} + \overbrace{\mathrm{HO,\ H_2N,\ C_{20}H_{14}O_5}}^{\text{Hydrated Camphoramic Acid.}};\ \text{and}$$

$$\overbrace{\mathrm{HO,\ H_2N,\ C_{20}H_{14}O_5}}^{\text{Hydrated Camphoramic Acid.}} = 2\,\mathrm{HO} + \overbrace{\mathrm{HN,\ C_{20}H_{14}O_4}}^{\text{Camphorimide.}}.$$

The theory of the existence of amidogen and imidogen as distinct organic groups or radicles in these different bodies, does not, upon a general view of the question, appear to have any ve probability. It was, indeed, proposed merely as a tempor dient for representing the facts. The different groups desi amides, imides, and nitriles, must rather be regarded as *res* results of successive stages of dehydration. The terms tl may, however, be conveniently retained, provided that th not taken to imply an adhesion to the theory in accord which these names were framed.

We may sum up the foregoing facts in the following The compounds which correspond to the neutral ammonia

1. The *amides*, produced by the combination of the l a monobasic acid with 1 equivalent of ammonia, and the tion of 2 equivalents of water.

2. The *diamides*, produced by the combination of 1 c of the hydrated dibasic acid with 2 equivalents of attended by the separation of 4 equivalents of water.

3. The *nitriles*, produced by a combination of 1 equ a hydrated monobasic acid and 1 of ammonia, minus 4 HO 1 equivalent of the hydrate of a dibasic acid and 2 equi ammonia, minus 8 equivalents of water.

The compounds which correspond to the acid amm are :—

4. *Amidated acids*, formed from 1 equivalent of the of a dibasic acid and 1 of ammonia, minus 2 HO.

5. *Imides*, formed from 1 equivalent of a hydrated dil and one of ammonia, with elimination of 4 HO.

(1049) *Hydramides.*—Besides the varieties of amide mentioned, a particular class of compounds is formed by t of ammonia upon certain volatile oils, which appear to l the group of aldehyds. These bodies, termed ***hydramides*** [illegible] by the union of 3 equivalents of the volatile oil an [illegible] of ammonia, while 6 equivalents of water are s [illegible] of this kind are formed with the essential oils [illegible] of spiræa, of cinnamon, of cummin, and of anise

[illegible] Hydrobenzamide.

$$[illegible] + 2(H_3N) = \overbrace{C_{42}H_{18}N_2} + 6\ H$$

[illegible] Salhydramide.

$$[illegible] + 2(H_3N) = \overbrace{C_{42}H_{18}N_2O_6} + 6\ H$$

[illegible] Anishydramide.

$$[illegible] + 2(H_3N) = \overbrace{C_{48}H_{24}N_2O_6} + 6\ H$$

[illegible] hydrogen in acting upon the hydramides, [illegible] analogous to the essences from which th originally obtained; but the new essences contain as many equivalents of sulphur as they previously had lost of oxygen, the ammonia being separated in the form of hydrosulphate; thus, thiobenzole is obtained from hydrobenzamide, and thiosalicole from salhydramide:—

$$\overbrace{C_{42}H_{18}N_2}^{\text{Hydrobenzamide.}} \quad + \quad 6\,HS \quad = \quad 2\,(H_3N) \quad + \quad 3\,\overbrace{(C_{14}H_6S_2,\ H)}^{\text{Thiobenzole.}};$$

$$\overbrace{C_{42}H_{18}N_2O_6}^{\text{Salhydramide.}} \quad + \quad 6\,HS \quad = \quad 2\,(H_3N) \quad + \quad 3\,\overbrace{(C_{14}H_6S_2O_2,\ H)}^{\text{Thiosalicole.}}.$$

(1050) *Preparation and properties of the Amides.*—The amides may be prepared by various methods:—

1. They may be obtained by the simple distillation of the ammoniacal salts, in the manner practised by Dumas for procuring oxamide from oxalate of ammonia.

2. Liebig, in the preparation of the amides, takes advantage of the reaction which occurs when the compound ethers are mixed with ammonia, which may be employed in the form either of an aqueous or of an alcoholic solution. The result of this decomposition is the formation of an alcohol, and of the amide of the acid contained in the ether; for example:—

$$\overbrace{2\,C_4H_5O,\ C_4O_6}^{\text{Oxalic Ether.}} + \overbrace{2\,(H_3N)}^{\text{Ammonia.}} = \overbrace{2\,(C_4H_5O,\ HO)}^{\text{Alcohol.}} + \overbrace{2\,(H_2N)\ C_4O_4}^{\text{Oxamide.}}.$$

This method is far superior to the first; it is of more general application, and the results which it yields are perfectly definite, being produced by a specific mode of double decomposition. Sometimes the reaction does not occur immediately; it may in such cases be facilitated by inclosing the ammonia and ether in a sealed tube, and exposing the mixture for some hours to a temperature of 212°. In this manner benzamide is obtained speedily, although it requires many weeks at the ordinary temperature to effect the decomposition. If other alkalies analogous to ammonia be substituted for the ammonia in this reaction, compounds analogous to amides are formed: thus, if aniline, or methylia, or ethylia, be mixed with oxalic ether, oxanilide, oxamethylide, or oxethylide, will be formed, thus:—

$$\overbrace{2\,C_4H_5O,\ C_4O_6}^{\text{Oxalic Ether.}} + \overbrace{2(C_{12}H_5,\ H_2N)}^{\text{Aniline.}} = \overbrace{2(C_4H_5O,\ HO)}^{\text{Alcohol.}} + \overbrace{2(H,\ C_{12}H_5,\ N)\ C_4O_4}^{\text{Oxanilide.}};$$

$$\text{and } \overbrace{2\,C_4H_5O,C_4O_6}^{\text{Oxalic Ether.}} + \overbrace{C_4H_5,\ H_2N}^{\text{Ethylia.}} = \overbrace{2(C_4H_5O,\ HO)}^{\text{Alcohol.}} + \overbrace{2\,(H,\ C_4H_5,\ N)\ C_4O_4}^{\text{Oxethylide.}}.$$

3. Gerhardt and Chiozza prepare many of the amides with facility, by treating the solid sesquicarbonate of ammonia with the oxychlorides (1097) which correspond to the anhydrides (1099) of

those acids of which the amides are required. This process is very advantageous when applied to the preparation of amides which are insoluble or sparingly soluble in water, such as benzamide and cuminamide: all that is required in the performance of the operation is to triturate the carbonate of ammonia in a mortar with the oxychloride; after which the amide is formed by gently warming the mass; carbonic acid escapes with effervescence, and the sal-ammoniac and excess of carbonate of ammonia are removed by washing with water. Cuminamide, for instance, is formed by the following reaction:—

$$\overbrace{C_{20}H_{11}O_2Cl}^{\text{Cuminic Oxychloride.}} + \overbrace{2H_4NO,\ 3\,CO_2}^{\text{Sesquicarb. Ammonia.}} = \overbrace{H_2NC_{20}H_{11}O_2}^{\text{Cuminamide.}} + 3CO_2 + \overbrace{H_4NCl}^{\text{Hydrochlor. Ammonia.}} + 2HO.$$

The amides of acetic, propionic, butyric, valeric, and of a few other acids are freely soluble in water, and have a sweet taste; but the amides, as a class, are either sparingly soluble or quite insoluble. Those which are soluble in water are also generally dissolved by alcohol and ether. By long boiling with water most of them become dissolved, and converted into ordinary salts of ammonia, by the assumption of the elements of water. This change is greatly accelerated by the addition of a minute quantity of any free acid. The presence of a free alkali produces a like transformation; if potash or soda be the base employed, salts of these alkalies are formed, whilst ammonia is liberated: this change occurs very slowly at ordinary temperatures, but it takes place rapidly at the boiling point.

(1051) *Theory of the Amides.*—The amides, ever since their discovery, have offered interesting subjects of investigation and speculation to the chemist. They are substances which, although derived from ammonia, exhibit no basic power; yet the hydramides can be converted into compounds which possess all the properties of powerful alkalies (1068).

Gerhardt and Chiozza have recently published a valuable memoir upon the amides (*Ann. de Chimie*, III. xlvi. 129), in which they endeavour to show that these bodies bear the same relation to their respective acids, that the volatile alkalies, methylia, ethylia, &c., do to the alcohols from which they are formed. The amides, when treated with nitrous acid, yield nitrogen and the acid from which the amide was obtained; and under similar treatment the volatile alkalies of the alcohols yield nitrogen and their corresponding alcohol. Upon this view, therefore, the amides are compounds derived by substitution from ammonia, upon which as a type they are founded; the ordinary amides of the monobasic acids, such as benzamide, being ammonia in which the basic character is neutralized by the substitution of an electro-negative radicle (such as benzoyl) for one of its equivalents of hydrogen: thus, ammonia being $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$, benzamide ($C_{14}H_7O_2N$) would be $\left.\begin{matrix}C_{14}H_5O_2\\H\\H\end{matrix}\right\}N$; and starting from this idea, Gerhardt and Chiozza were led to effect upon the amides a series of substitutions similar to those performed by Hofmann with ethylia and its homologues. In this manner they were enabled by double decomposition to obtain amides, in which one atom, or two atoms of hydrogen were displaced by certain electro-negative bodies; these electro-negative bodies being compounds, which when substituted for either one half or both halves of the hydrogen in the double molecule of water, furnish in one case, the hydrated, in the other, the anhydrous acids (1099):—benzoyl ($C_{14}H_5O_2$), for instance, when thus substituted for hydrogen, yields either benzoic acid or benzoic anhydride:—

$$\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_{14}H_5O_2\\H\end{matrix}\right\}O_2}^{\text{Benzoic Acid.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_{14}H_5O_2\\C_{14}H_5O_2\end{matrix}\right\}O_2}^{\text{Benzoic Anhydride.}}$$

Now, it has been already explained, that the various compounds formed upon a certain type may possess properties in which they gradually differ from those that precede and from those that follow them in the series; these differences depending upon the nature and number of equivalents of the elements or compounds which are introduced by processes of substitution into the prototype of the series (917). It becomes, therefore, quite possible to obtain compounds formed upon the type or plan of an eminently basic substance like ammonia, which, nevertheless, may possess neutral or even well-marked acid characters. In this manner Gerhardt and Chiozza have by substitution formed various classes of amides which they distinguish thus:—

1. *Primary amides,* or amides which like acetamide $(C_4H_5O_2N) = \left.\begin{matrix}C_4H_3O_2\\H_2\end{matrix}\right\}N$, represent a molecule of ammonia, in which a single equivalent of hydrogen is displaced by an organic radicle.*

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* If a monobasic acid be defined to be an acid representing a double molecule of water $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$, in which 1 equivalent of hydrogen is displaced by an electro-negative radicle (acetic acid being $\left.\begin{matrix}C_4H_3O_3\\H\end{matrix}\right\}O_2$), the primary amide is the amide derived from the neutral ammonia salt of such an acid.

2. *Secondary amides,* in which the displacement of hydrogen in the molecule of ammonia extends to two equivalents; such for example as cumylsalicylamide ($C_{34}H_{17}O_6N$), or $\left.\begin{cases} C_{14}H_5O_4 \\ C_{20}H_{11}O_2 \\ H \end{cases}\right\} N$.

3. *Tertiary Amides,* in which each equivalent of the hydrogen of the ammonia is displaced by an equivalent of an organic radicle; such as dibenzo-sulphophenylamide* ($C_{40}H_{15}S_2O_8N$), or $\left.\begin{cases} C_{14}H_5O_2 \\ C_{14}H_5O_2 \\ C_{12}H_5,2SO_2 \end{cases}\right\} N$.

The imides may be regarded as belonging to the class of secondary amides, but the two equivalents of hydrogen in the ammonia are displaced by an indivisible group equivalent to H_2 in combination. Succinimide ($C_8H_5O_4N$), for example, may be represented as $\left.\begin{matrix} C_8H_4O_4 \\ H \end{matrix}\right\} N$. The dibasic radicle of the succinic acid in this case, has displaced two equivalents of the hydrogen of the ammonia. But it would probably be more correct to double the formula of the imides, and to refer them to a class of amides termed *diamides,* which are derived from a double equivalent of ammonia (H_6N_2).

If this were done, the three different amides of succinic acid (2 HO, $C_8H_4O_6$) would all belong to the class of diamides:—

1. Succinamide, $C_8H_8O_6N_2$. $= \left.\begin{cases} C_8H_4O_4 \\ H_2 \\ H_2 \end{cases}\right\} N_2$;

2. Bisuccinamide, or succinimide $C_{16}H_{10}O_8N_2$, or $2(C_8H_5O_4N)$ $= \left.\begin{cases} C_8H_4O_4 \\ C_8H_4O_4 \\ H_2 \end{cases}\right\} N_2$;

3. Trisuccinamide, (diamide of succinyl) $C_{24}H_{12}O_{12}N_2$ . . $= \left.\begin{cases} C_8H_4O_4 \\ C_8H_4O_4 \\ C_8H_4O_4 \end{cases}\right\} N_2$.

The secondary amides may be prepared by heating the primary amides to a certain temperature with an equivalent quantity of the electro-negative oxychloride: hydrochloric acid escapes in abundance, and the secondary amide is found in the residue. Care must be taken to prevent the temperature from rising too high, otherwise nitriles are apt to be formed. If the products of the reaction assume a viscous form, they must not be dissolved whilst in this state; but must be allowed to become solid; their solidification may often be effected by the addition of a few drops of ether. The formation of cumylsalicylamide by treating chloride of cumyl (cuminic oxychloride) with salicylamide, offers an instance of the formation of a secondary amide in this manner:—

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* The inharmonious and unwieldy names employed to designate these complicated substitution products are apt to discourage the learner; but in the present state of chemical nomenclature they are almost necessary, for the purpose of pointing out the parentage and relationship of the bodies which they represent; since the compounds themselves have little or no intrinsic interest, the rel[illegible]icated being, in most cases, the really important circumstances.

$$\overbrace{\left.\begin{matrix}C_{14}H_5O_4\\H\\H\end{matrix}\right\}N}^{\text{Salicylamide.}} + \overbrace{\left.\begin{matrix}C_{20}H_{11}O_2\\Cl\end{matrix}\right\}}^{\text{Chloride of Cumyl.}} = \overbrace{\left.\begin{matrix}C_{14}H_5O_4\\C_{20}H_{11}O_2\\H\end{matrix}\right\}N}^{\text{Cumylsalicylamide.}} + \overbrace{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}^{\text{Hydrochloric Acid.}}.$$

Sometimes new amides may be obtained by heating together two primary amides in equivalent proportions; ammonia is then disengaged, and a secondary amide is formed. For example:—

$$\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\H\\H\end{matrix}\right\}N}^{\text{Benzamide.}} + \overbrace{\left.\begin{matrix}C_{14}H_5O_4\\H\\H\end{matrix}\right\}N}^{\text{Salicylamide.}} = \overbrace{\left.\begin{matrix}C_{14}H_5O_2\\C_{14}H_5O_4\\H\end{matrix}\right\}N}^{\text{Benzoyl Salicylamide.}} + \overbrace{\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N}^{\text{Ammonia.}}$$

The secondary amides possess the acid character more strongly than the primary amides; and they frequently form metallic salts, those which contain silver being the salts most readily procured. Thus benzosulphophenylamide, when dissolved in boiling water by the aid of a few drops of ammonia, and mixed with a boiling solution of nitrate of silver, yields a compound in which silver takes the place of hydrogen in the original amide, the new silver salt crystallizing out in groups of colourless needles:—

$$\overbrace{\left.\begin{matrix}C_{12}H_5,\ 2\,SO_2\\C_{14}H_5O_2\\H\end{matrix}\right\}N}^{\substack{\text{Benzosulpho-}\\\text{phenylamide.}}} + \overbrace{\left.\begin{matrix}NO_4\\Ag\end{matrix}\right\}O_2}^{\substack{\text{Nitrate of}\\\text{Silver.}}} = \overbrace{\left.\begin{matrix}C_{12}H_5.\ 2\,SO_2\\C_{14}H_5O_2\\Ag\end{matrix}\right\}N}^{\substack{\text{Benzosulphophenyl-}\\\text{argentamide.}}} + \overbrace{\left.\begin{matrix}NO_4\\H\end{matrix}\right\}O_2}^{\text{Nitric Acid.}}$$

The tertiary amides are readily prepared from such silver salts of the secondary amides; for they are attacked by the negative oxychlorides even without the aid of heat, double decomposition occurring, whilst chloride of silver is formed, and an organic radicle takes the place of the silver in the amide. The silver compound just described, is thus, by the action of chloride of benzoyl, readily converted into dibenzosulphophenylamide:—

$$\overbrace{\left.\begin{matrix}C_{12}H_5,\ 2\,SO_2\\C_{14}H_5O_2\\Ag\end{matrix}\right\}N}^{\substack{\text{Benzosulphophenyl-}\\\text{argentamide.}}} + \overbrace{\left.\begin{matrix}C_{14}H_5O_2\\Cl\end{matrix}\right\}}^{\substack{\text{Chloride}\\\text{of Benzoyl.}}} = \overbrace{\left.\begin{matrix}C_{12}H_5,\ 2\,SO_2\\C_{14}H_5O_2\\C_{14}H_5O_2\end{matrix}\right\}N}^{\substack{\text{Dibenzosulpho-}\\\text{phenylamide.}}} + \left.\begin{matrix}Ag\\Cl\end{matrix}\right\}$$

When the silver salt of a secondary amide, such as the one referred to in the last equation, is treated with ammonia, it is commonly dissolved without fixing the elements of water, but it combines with the ammonia and forms a diamide, that is to say, an amide derived from two molecules of ammonia; for example:—

$$\left.\begin{matrix} C_{12}H_5,\ 2\,SO_2 \\ C_{14}H_5O_2 \\ Ag \end{matrix}\right\}N \;+\; H_3N \;=\; \left.\begin{matrix} C_{12}H_5,\ 2\,SO_2 \\ C_{14}H_5O_2 \\ Ag \\ H_3 \end{matrix}\right\}N_2 \quad .$$

The other secondary and tertiary amides when treated with ammonia, have the power of fixing the elements both of ammonia and of water so as to form amidated acids, or rather salts of ammonia with amidated acids. Thus, for instance, benzosulphophenylamide may be transformed by ammonia into benzosulphophenylamate of ammonia:—

$$2\left(\left.\begin{matrix} C_{12}H_5,\ 2\,SO_2 \\ C_{14}H_5O_2 \\ H \end{matrix}\right\}N\right) + H_3N + 4\,HO = \left(\,H_4NO,\ C_{52}H_{25}N_2S_4O_{15}\,\right)$$

The description of a few of the more interesting compounds belonging to the different classes of amides will suffice to give an idea of the general properties of these compounds.

(*a*) *Amides of the Monobasic Acids.*

(1052) *Acetamide* $\left(\left.\begin{matrix} C_4H_3O_2 \\ H_2 \end{matrix}\right\}N = C_4H_5NO_2\right)$.—This compound is obtained in abundance by decomposing acetic ether with an equal volume of aqueous solution of ammonia, under pressure, and at a temperature of 250° or 260°. It forms a white solid which fuses at 172° and boils at 430°. It crystallizes after fusion. Acetamide is soluble in water and has a cooling sweetish taste. When distilled with phosphoric acid it loses two equivalents of water, and becomes converted into acetonitrile. If the acetic ether be decomposed with ethylia, it forms a corresponding compound, *ethylacetamide* or *aceto-ethylide* $C_8H_9NO_2 = \left.\begin{matrix} C_4H_3O_2 \\ C_4H_5 \\ H \end{matrix}\right\}N$.

Ethyl-diacetamide $C_{12}H_{11}NO_4 = \left.\begin{matrix} 2\,(C_4H_3O_2) \\ C_4H_5 \end{matrix}\right\}N$, is a limpid, colourless, neutral liquid, which boils at 377°. It is obtained by heating cyanic ether with acetic anhydride to about 392°, in a sealed tube. Carbonic acid escapes on opening the tube when cold:—

$$\overbrace{C_4H_5O,\ C_2NO}^{\text{Cyanate of Ethyl.}} + \overbrace{2(C_4H_3O_3)}^{\text{Acetic Anhydride.}} = 2\,CO_2 + \overbrace{C_{12}H_{11}NO_4}^{\text{Ethyldiacetamide.}}.$$

Trichloracetamide, $C_4H_2Cl_3NO_2 = \left.\begin{matrix} C_4Cl_3O_2 \\ H_2 \end{matrix}\right\}N$, is the compound obtained by decomposing trichloracetic ether with ammonia; but it is also obtained by acting upon several other perchlorinated ethylic ethers, such as the perchlorinated formic, carbonic, oxalic, and succinic ethers: perchloraldehyd likewise yields it when treated with ammonia. It is a crystallizable compound with a sweet taste; it melts at 275°, and is very soluble in alcohol and in ether.

(1053) *Propionamide* $C_6H_7NO_2$, *Butyramide* $C_8H_9NO_2$, and *Valeramide* $C_{10}H_{11}NO_2$, may all be obtained by the action of ammonia upon their respective ethers. They are fusible, volatile compounds, which may be sublimed without decomposition; they are soluble in water, alcohol, and ether. When distilled with anhydrous phosphoric acid, they yield the nitriles of the acid, or the hydrocyanic ether of the alcohol below them:—

$$\overbrace{C_6\,H_7\,NO_2}^{\text{Propionamide.}} \;-\; 2\,HO \;=\; \overbrace{C_6\,H_5N}^{\text{Propionitrile.}}\ (\text{or}\ \overbrace{C_4\,H_5,\,C_2N}^{\text{Cyanide of Ethyl.}})$$

$$\overbrace{C_8\,H_9\,NO_2}^{\text{Butyramide.}} \;-\; 2\,HO \;=\; \overbrace{C_8\,H_7N}^{\text{Butyronitrile.}}\ (\text{or}\ \overbrace{C_6\,H_7,\,C_2N}^{\text{Cyanide of Trityl.}})$$

$$\overbrace{C_{10}H_{11}\,NO_2}^{\text{Valeramide.}} \;-\; 2\,HO \;=\; \overbrace{C_{10}H_9N}^{\text{Valeronitrile.}}\ (\text{or}\ \overbrace{C_8\,H_9,\,C_2N}^{\text{Cyanide of Tetryl.}})$$

(1054) *Benzamide* $(C_{14}H_7NO_2)$ is a white solid, fusible at 239°, which may be sublimed without undergoing decomposition. It is sparingly soluble in water, but is more readily dissolved by alcohol and by ether, from which it crystallizes in right rhomboidal prisms. When boiled with free acid or alkali, it is quickly converted into benzoate of ammonia. Benzamide is most easily obtained by heating an alcoholic solution of ammonia with benzoic ether for some hours in a sealed tube. When boiled with red oxide of mercury, water is separated, and *hydrargo-benzamide* is obtained;

$$C_{14}H_7NO_2 + HgO = C_{14}H_6HgNO_2 + HO.$$

Hydrargo-benzamide may be viewed as $\left.\begin{matrix}C_{14}H_5O_2\\ Hg\\ H\end{matrix}\right\}N$, or benzamide in which the second equivalent of hydrogen has been displaced by mercury. Benzamide, when heated with potassium, loses oxygen; hydrogen is eliminated and benzonitrile is formed:—

$$C_{14}H_7NO_2 + K = C_{14}H_5N + H + KO,HO.$$

(*b*) *Nitriles.*

(1055) *Benzonitrile* $(C_{12}H_5N)$. *Sp.gr. of liquid* 1·007, *of vapour* 3·70.—This substance is a colourless oil, with a powerful odour of bitter almonds. It is sparingly soluble in water, but is miscible with alcohol and ether in all proportions. It boils at 376°, and emits an inflammable vapour, which burns with a smoky flame. It is readily obtained by the dry distillation of benzoate of ammonia, or of benzamide; and when washed with hydrochloric acid, and re-distilled, is obtained pure. Benzamide also yields benzonitrile when treated with chloride of benzoyl:—

$$\overbrace{C_{14}H_7NO_2}^{\text{Benzamide.}} + \overbrace{C_{14}H_5O_2Cl}^{\text{Chloride of Benzoyl.}} = \overbrace{C_{14}H_5N}^{\text{Benzonitrile.}} + \overbrace{HO, C_{14}H_5O_3}^{\text{Benzoic Acid.}} + HCl.$$

Benzonitrile, when boiled with alkalies, or with concentrated acids, is converted into benzoic acid and ammonia, with assimilation of the elements of water.

Cumonitrile ($C_{20}H_{11}N$, *Sp. gr. of liquid* 0·765) may be obtained by similar methods from cuminate of ammonia. It has a fragrant odour, and boils at 462°.

The nitriles of the fatty acids are identical with the hydrocyanic ethers of the alcohol in the series immediately below that of the acid from which they are obtained (997).

(*c*) *Amides of Dibasic Acids—Diamides.*

The dibasic acids give rise to the formation of diamides; that is to say, to amides formed from two equivalents of ammonia. We shall examine those of two acids only, viz., the amides of oxalic acid and those of succinic acid. The latter afford an instructive illustration of the preparation and properties of primary, secondary, and tertiary diamides, from the same acid.

(1056) *Oxamide*, $H_2NC_2O_2$; or $2\ (H_2N)C_2O_4 = \left.\begin{matrix}C_4O_4\\ H_2\\ H_2\end{matrix}\right\}N_2.$

This interesting compound is most readily obtained by decomposing oxalic ether by an aqueous or an alcoholic solution of ammonia. It may also be procured, though less advantageously, by distilling oxalate of ammonia, when it condenses in the neck of the retort and in the receiver in the form of white flocculi. Oxamide is a light tasteless powder, which is insoluble in cold water, but soluble to a small extent in boiling water, from which it is deposited on cooling in crystalline flakes. The solution is neutral and gives no precipitate with salts of lime. It is insoluble in alcohol. It may be sublimed in an open tube, though with difficulty. When its vapour is transmitted through a red-hot tube, it is decomposed, according to Liebig, into bicarbonate of ammonia, hydrocyanic acid, oxide of carbon, and urea:—

$$2\,\overbrace{[(H_2N)_2C_4O_4]}^{\text{Oxamide.}} = \overbrace{H_3N,\ 2\,CO_2}^{\text{Bicarb. Ammon.}} + H,\ C_2N + 2\,CO + \overbrace{H_4N_2C_2O_2}^{\text{Urea.}}$$

When oxamide is heated to 436°, in a sealed tube with water, it becomes transformed into oxalate of ammonia. The same change is effected by boiling oxamide with dilute acids or alkalies. If heated alone in closed vessels to 590°, it is converted into a mixture of cyanogen, oxide of carbon, and carbonate of ammonia. Oxamide, in fact, contains the elements of cyanogen and water; $(H_2N)_2C_4O_4 = 2\,(C_2N) + 4\,HO$; but the water reacting upon a portion of oxamide, converts it into oxalate of ammonia, and this, by the action of heat, is resolved into carbonate of ammonia and oxide of carbon:—

$$\overbrace{(H_2N)_2C_4O_4}^{\text{Oxamide.}} + 4\,HO = \overbrace{2\,H_4NO,\ C_4O_6}^{\text{Oxalate of Ammonia.}};\ \text{and}$$

$$\overbrace{2\,H_4NO,\ C_4O_6}^{\text{Oxal. Ammonia.}} = \overbrace{2\,(H_4NO,\ CO_2)}^{\text{Carb. Ammonia.}} + 2\,CO.$$

When oxamide is boiled with red oxide of mercury, the two bodies enter into combination, and form a white heavy powder $[HgO,\ (H_2N)_2C_4O_4]$.

If oxalic ether be decomposed by the alcohol alkalies, such as ethylia, methylia, and amylia, or by other bases, such as aniline, compounds are obtained corresponding to oxamide: thus ethylia, when made to act upon oxalic ether, yields diethyloxamide $(C_{12}H_{12}N_2O_4) = \left.\begin{matrix} C_4O_4 \\ 2\,(C_4H_5) \\ H_2 \end{matrix}\right\}N_2$; and aniline, under similar circumstances produces diphenyloxamide (oxanilide) $C_{28}H_{12}N_2O_4$:—

$$\overbrace{2\,C_4H_5O,\ C_4O_6}^{\text{Oxalic Ether.}} + \overbrace{2\,(C_{12}H_5,\ H_2N)}^{\text{Aniline.}} = \overbrace{2\left.\begin{matrix} C_4O_4 \\ (C_{12}H_5) \\ H_2 \end{matrix}\right\}N_2}^{\text{Oxanilide.}} + \overbrace{2\,(C_4H_5O,\ HO)}^{\text{Alcohol.}}.$$

(1057) *Succinamide* $\left(C_8H_8N_2O_4 = \left.\begin{matrix} C_8H_4O_4 \\ H_2 \\ H_2 \end{matrix}\right\}N_2\right)$. When succinic ether is mixed with twice its volume of a concentrated solution of ammonia, alcohol is liberated, and succinamide is deposited in the form of a granular crystalline compound. It is nearly insoluble in cold water, but is dissolved by boiling water in considerable quantity. Alcohol and ether do not dissolve it.

Succinimide, or ***bisuccinamide*** $2\,(C_8H_5NO_4,\ 2\ Aq) = 2(C_8H_4O_4)H_2N_2 + 4\ Aq$.—The simplest method of procuring this compound consists in neutralizing a solution of succinic acid with ammonia, evaporating to dryness, and submitting the residue to distillation. It may also be obtained by causing dry ammonia to react upon anhydrous succinic acid; during this reaction water is formed, and a considerable elevation of temperature occurs:—

$$\overbrace{2\,(C_8H_4O_6)}^{\text{Succinic Anhydride.}} + 2\,(H_3N) = \overbrace{\left.\begin{matrix}C_8H_4O_4\\C_8H_4O_4\\H_2\end{matrix}\right\}N_2}^{\text{Succinimide.}} + 4\,HO.$$

When succinamide is heated, ammonia is evolved, and succinimide is formed:—

$$\overbrace{2\,(C_8H_8N_2O_4)}^{\text{Succinamide.}} = 2\,(H_3N) + \overbrace{C_{16}H_{10}N_2O_8.}^{\text{Succinimide.}}$$

When crystallized from its aqueous solution, succinimide forms beautiful, efflorescent, rhombic tables. It is freely soluble in water, and the solution has a weak acid reaction; alcohol also dissolves it, but it is insoluble in ether; it fuses at 410°. Succinimide is metameric with succinamic acid. It yields a crystallizable compound with silver, termed ***succinimidate of silver***, $\left.\begin{matrix}C_8H_4O_4\\C_8H_4O_4\\Ag_2\end{matrix}\right\}N_2\ [= 2(C_8H_4AgNO_4)]$; this body is obtained in needles by mixing a boiling concentrated alcoholic solution of succinimide, rendered slightly alkaline by ammonia, with a hot alcoholic solution of nitrate of silver: the salt is deposited as the liquid cools. It is not decomposed by potash in the cold, but on the application of heat to the mixture, ammonia is evolved. Succinimidate of silver is freely soluble in ammonia, and if the solution so obtained be left to spontaneous evaporation, a syrupy alkaline liquid is left, which gradually becomes converted into a mass of rectangular prisms $[2\,(C_8H_4AgNO_4)\ 2\ H_3N]$, from which potash immediately liberates ammonia. Succinimidate of silver is decomposed with explosion when suddenly heated: it is isomeric with succinamate of silver, into which it is converted if its ammoniacal solution be boiled for some time; it then becomes much more soluble, and is no longer explosive.

Trisuccinamide $C_{24}H_{12}O_{12},\ N_2 = 3\ (C_8H_4O_4)N_2$.—When an equivalent of succinic oxychloride (1182) is dissolved in twice its volume of ether, and mixed with an equivalent of the succinimidate of silver, an immediate reaction occurs, sufficient heat is emitted to volatilize the ether, and chloride of silver is formed:—

$$\overbrace{2\,(C_8H_4O_4)\,Ag_2N_2}^{\text{Succinimidate of Silver.}} + \overbrace{C_8H_4O_4Cl_2}^{\text{Succinic Oxychloride.}} = \overbrace{3\,(C_8H_4O_4)\,N_2}^{\text{Trisuccinamide.}} + 2\,AgCl.$$

Boiling ether dissolves it under pressure, and deposits small crystals, which are fusible at 181°. Water and alcohol decompose this compound, alcohol converting it into succinimide without the formation of succinic ether.*

(*d*) *Amidated Acids.*

A single instance will sufficiently illustrate the nature of these bodies, after what has been already stated of their general properties: but the existence of this class of substances is not confined to the compounds of organic chemistry, since both sulphuric and carbonic acids yield amidated acids, viz., the sulphamic and carbamic

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* Wurtz has put forward a view of the amides differing from the foregoing one, inasmuch as he proposes to consider the monobasic amides as formed from the type of the double molecule of water $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$, and thus to connect them with the acids: for example, if acetic acid in its hydrated form be written $\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2$, the amides of acetic acid would be thus indicated:—

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}HN}^{\text{Acetamide.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}(C_4H_5)N}^{\text{Ethylacetamide.}} \quad ;$$

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}HN}^{\text{Diacetamide.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}(C_4H_5)N}^{\text{Ethyldiacetamide.}} \quad .$$

It will be seen that upon this theory the amides are supposed to be formed by the action of ammonia upon the hydrated acids; H_3N, losing two equivalents of hydrogen, which combine with the two exterior equivalents of oxygen, while the residue HN takes the place of the oxygen thus removed.

Wurtz considers, with Gerhardt, that the dibasic acids are derived from two double molecules of water (1102), and their relation to their amides and amidated acids admits of being very simply traced: for example—

$$\overbrace{\left.\begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}O_2\\\left.\begin{matrix}H\\H\end{matrix}\right\}O_2\end{matrix}\right\}}^{\text{Water.}} ; \overbrace{\left.\begin{matrix}\left.\begin{matrix}C_2O_2\\H\end{matrix}\right\}O_2\\\left.\begin{matrix}C_2O_2\\H\end{matrix}\right\}O_2\end{matrix}\right\}}^{\text{Oxalic Acid.}} ; \overbrace{\left.\begin{matrix}\left.\begin{matrix}C_2O_2\\H\end{matrix}\right\}HN\\\left.\begin{matrix}C_2O_2\\H\end{matrix}\right\}HN\end{matrix}\right\}}^{\text{Oxamide.}} ; \overbrace{\left.\begin{matrix}\left.\begin{matrix}C_2O_2\\H\end{matrix}\right\}O_2\\\left.\begin{matrix}C_2O_2\\H\end{matrix}\right\}HN\end{matrix}\right\}}^{\text{Oxamic Acid.}} .$$

This view is ingenious, but it does not account for the fact that oxamide is neutral, and that oxamic acid is monobasic, whilst oxalic acid is intensely acid and dibasic. The two equivalents of hydrogen which are here represented as occupying similar positions in oxalic acid, in oxamide and in oxamic acid in each case, certainly perform the functions of a base in oxalic acid; if the theory be correct, they also must occupy a basic position in the other compounds, and as such should be exchangeable with a metal: but on making the experiment this exchange is found not to take place.

acids; these bodies being produced by the reaction of dry ammonia upon anhydrous sulphuric, and carbonic acids; the compounds to which the term of ammonides was applied (507) being supposed by Laurent and Gerhardt to be amidated salts of

(1058) *Oxamic Acid* ($C_4H_3NO_6$ = HO, H_2 binoxalate of ammonia is exposed to a carefully loses its water of crystallization, and begins to u sition at a temperature of about 430°, giving of acid, formic acid, and carbonic oxide. The resid if not heated too strongly, consists of oxamide a stance soluble in water. This soluble compound is may be neutralized by baryta water, or by lime crystalline salts of these bases on evaporating the aqueous solution be boiled, it is reconverted i ammonia; HO, H_2N, $C_4O_5 + 2$ HO = HO, H_4NO,

A large number of dibasic acids form compou oxamic acid, such as the following:—

Sulphamic Acid? . . .	HO, H_2N, S
Carbamic Acid? . . .	HO, H_2N, C
Lactamic Acid . . .	HO, H_2N, C
Tartramic Acid . . .	HO, H_2N, C
Malamic Acid	HO, H_2N, C_8
Phthalamic Acid . . .	HO, H_2N, C_1
Camphoramic Acid . .	HO, H_2N, C_{20}

Monday — [illegible]
Tuesday — [illegible]
Wednesday — [illegible]
Thursday — [illegible]
Friday — [illegible]
Saturday — [illegible]

§ II. The Organic Bases.

(1059) The Alkaloids, or *organic alkalies*, are not less numerous than the organic acids: they form a natural group of high interest to the chemist, not only on account of their remarkable composition, but also from their powerful effects as medicinal or poisonous agents upon the animal economy.

In the majority of instances the natural organic bases are derived from the vegetable kingdom, and constitute the active principle of the plant that contains them. They always occur in combination with some acid, which is also frequently of organic origin, and peculiar to the plant or family of plants in which it is found. In many cases the alkaloids which occur in one species of a natural family are found also in several of the other members of the same family.

The vegetable bases when in solution have generally a decidedly alkaline reaction upon test papers, and they for the most part completely neutralize the acids, forming definite and well crystallized salts.* They obey the usual law of bases when their salts are submitted to electrolytic analysis; since under these circumstances the base is liberated at the platinode of the voltaic battery. Most of these bases are dissolved sparingly by water, but are more freely soluble in alcohol, especially when it is at a boiling temperature; the alcoholic solutions as they cool generally deposit the alkaloids in the crystalline form. Some of these bases occur in two isomeric conditions, one of which is crystallizable, and the other amorphous; both forms combine with acids in the same proportion, but the crystalline variety alone yields crystalline salts.

The vegetable or organic bases may be subdivided into two well-marked classes:—1st. Those which like aniline ($C_{12}H_7N$), do not contain oxygen:—and 2nd. Those which like quinia ($C_{40}H_{24}N_2O_4$, *6* aq) do contain it. The bases of the first class are oily and volatile; they rapidly absorb oxygen from the air; this class has recently been augmented by the formation of numerous artificial alkaloids, many of which closely resemble aniline in properties, and may, like aniline, be regarded as derivatives of ammonia. Less is known of the derivation and rational composition of the second and more complicated class of oxidized bases. All of the volatile bases have a powerful odour, and may be distilled either alone or with the vapour of water, without undergoing decomposition. Advantage is taken of this property in their preparation or extraction; it is sufficient to digest the plant containing them in a weak alkaline ley, and to submit the mixture to distillation. A portion of ammonia always comes over with the condensed products, which are neutralized by sulphuric acid, then evaporated, and afterwards digested with alcohol. This menstruum leaves the sulphate of ammonia, but dissolves the sulphate of the organic base, which may be purified by recrystallization. If this salt be agitated with a mixture of equal parts of a strong solution of hydrate of potash and ether, the mixture separates on standing into two layers, the upper one consisting of an ethereal solution

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* It is much to be regretted that a uniform system of nomenclature has not been adopted for these compounds; that the termination *ia*, for example, as in morphia and strychnia, has not been appropriated to the bases, to indicate their analogy with ammonia: the termination *ine*, might then have been restricted to the neutral principles. Both these terminations are now attached indifferently, by many writers, to the bases, and it might be attended with inconvenience were the attempt uniformly made to alter the termination familiarized by usage. In this work I have generally indicated the neutral bodies, such as salicin, amygdalin, &c., by the termination *in*, reserving the ending, *ine*, for those which have basic properties.

[illegible] a state of purity [illegible]

[illegible] of extracting the alkaloids which are not [illegible] powdered vegetable is digested with [illegible] acid, by which the organic salt is [illegible] and a [illegible] sulphate or chloride is [illegible] alumina, magnesia, or lime [illegible] precipitate of the impure [illegible] magnesia be used is mixed with [illegible] with an insoluble compound of the [illegible] The precipitate is treated with boiling [illegible] and the alkali generally crystallizes: [illegible] hydrochloric acid, digested with [illegible] The salt is purified by recrystallization [illegible] perfectly removes the colour, has [illegible] disadvantage of retaining also a [illegible] of the organic alkali: and if a great [illegible] almost the whole of the salt may be [illegible]

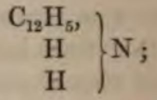
[illegible] organic bases are dissolved by chloroform: and [illegible] may [illegible] be taken advantage of for the [illegible] from their solutions:—The sub[illegible] is to be digested in a dilute [illegible]: the liquid is filtered if [illegible] with ammonia and agitated with [illegible] of its bulk of chloroform: the chloroform [illegible] separates in the form of a heavy oily layer, which can be [illegible] it will be found to contain nearly the whole of [illegible] base, which may afterwards be purified by the usual methods. [illegible] of operating often affords valuable aid in medico-legal [illegible] instituted for the purpose of detecting certain bases which [illegible] suspected to have been administered as poisons.

[illegible] *Nature of the Organic Bases.*—The composition of [illegible] vegetable alkalies is remarkable; all of them contain nitrogen, [illegible] the greater number each equivalent of base includes one [illegible] of nitrogen. Berzelius regarded ammonia as the com[illegible] renders upon them their basic character; and he con[illegible] to be compounds of ammonia with a variety of neu[illegible] which in most cases are not susceptible of isolation; [illegible] neutral principle or *colligate* with the ammonia being of the same intimate nature as that of alcohol with sulphuric acid in the sulphethylic acid, where neither of the constituents exhibits its ordinary characters. Thus quinia (halving the formula now adopted) ($C_{20}H_{12}NO_2$, 3 aq), was represented by Berzelius as ($C_{20}H_9O_2$, NH_4O), 2 aq, or as a compound of the colligate, $C_{20}H_9O_2$, with oxide of ammonium and water of crystallization. This mode of viewing the composition of certain vegetable bases acquires support from the discovery that, by the direct union of ammonia with a limited class of neutral substances, such as oil of mustard, and oil of bitter almonds, a number of basic compounds may be obtained, which present a striking analogy both in composition and properties to many of the organic bases produced by living plants: but though the theory of Berzelius may be admitted in particular cases, it does not appear to be generally applicable to the organic alkalies.

A different view was suggested several years ago by Liebig, who, finding that these bases gave no evidence of the presence of ammonia ready formed within them, suggested that they might be compounds containing H_2N, or amidogen; and that they might be derivatives from ammonia, in which an equivalent of hydrogen had been displaced by an organic group: he even predicted that if it should be found possible to displace this equivalent of hydrogen by ethyl, or by some electro-negative hydrocarbon, a powerful volatile base would probably be obtained. This sagacious conjecture has since been fully verified by the discoveries of Wurtz and Hofmann, who have succeeded in obtaining the very compounds anticipated by Liebig; and Hofmann, as we have already seen, has extended the process of substitution much further. Liebig's view, with the extension and modifications required by the progress of discovery in this direction, admits in many instances of being happily applied to the natural vegetable bases, since these bodies themselves can be subjected to operations analogous to those which are applied in the formation of the alcohol bases; and portions of the hydrogen which they contain may thus be displaced by basic hydrocarbons: for instance, conia, ($C_{16}H_{14}, H, N$), may be converted into ethyl-conia ($C_{16}H_{14}, C_4H_5, N$), by displacing an equivalent of hydrogen by one of ethyl. The number of exchangeable equivalents of hydrogen in the different bases depends upon the molecular constitution of the particular base under experiment.

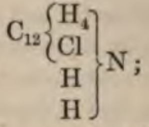
But the hydrocarbons either originally existing in the base or subsequently introduced into it, may also experience a change in their components by a species of secondary substitution by chlorine or bromine, whilst the general basic properties of the compound remain unchanged. Aniline ($C_{12}H_5, H_2N$) for example, may be represented as ammonia in which one equivalent of hydrogen is displaced by $C_{12}H_5$ (phenyl); but aniline may lose a part of its hydrogen, and receive chlorine in its place, without having its basic character destroyed, becoming chloraniline ($C_{12}H_4Cl, H_2N$): and even NO_4 may be substituted for a portion of the hydrogen in aniline, while the new body (nitraniline, $C_{12}H_4NO_4, H_2N$) still retains its power of forming salts with acids. Nitraniline affords an instance of the artificial formation of an alkaloid containing two equivalents of nitrogen; and examples of the occurrence of bases which contain more than one equivalent of nitrogen are not wanting among the products of organic nature. The relations of aniline to chloraniline and nitraniline, may be represented in the following manner:—

Aniline . . . . .



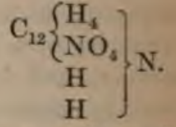
$$\left.\begin{matrix} C_{12}H_5, \\ H \\ H \end{matrix}\right\} N;$$

Chloraniline .



$$\left.\begin{matrix} C_{12}\begin{cases} H_4 \\ Cl \end{cases} \\ H \\ H \end{matrix}\right\} N;$$

Nitraniline .



$$\left.\begin{matrix} C_{12}\begin{cases} H_4 \\ NO_4 \end{cases} \\ H \\ H \end{matrix}\right\} N.$$

Hofmann in the course of his researches upon aniline, discovered another method of combination which is worthy of remark, since it explains a second mode in which an additional equivalent of nitrogen may be introduced into the alkaloid without increasing its basic power:—cyanogen unites directly with aniline, forming a body, the composition of which is represented by $C_{14}H_7N_2$, but which is evidently not a hydrocyanate of aniline (represented by the formula $C_{12}H_7N, HC_2N$), but a new body, cyaniline, which possesses basic properties, and enters into combination with acids in the proportion of one equivalent of acid to each equivalent of aniline which the new base contains.

It is evident that changes such as these affect that portion only of the compound which, like $C_{12}H_5$ in aniline, has been introduced into the ammonia by substitution; the compound retaining the basic power which it originally derived from the ammonia, upon the type of which it has been constructed. When this type is destroyed, the basic power of the compound disappears. For example, just as oxalate of ammonia, by the abstraction of the elements of four equivalents of water, loses its saline character, and becomes converted into an indifferent insoluble body, oxamide, and this by the further abstraction of four more equivalents of water furnishes cyanogen (1046); so oxalate of aniline, by losing four equivalents of water, becomes oxanilide; and by abstraction of four more equivalents of water becomes oxanilo-nitrile, or phenylocyanogen, which still retains an equivalent of nitrogen intimately combined both with carbon and hydrogen, but which has lost its relationship or homology with ammonia, and with it has also lost its basic character. Thus:—

$$\overbrace{2\,(C_{12}H_5,\ H_3NO)\ C_4O_6}^{\text{Oxalate of Aniline.}} = \overbrace{2\,(C_{12}H_5,\ HN)\ C_4O_4}^{\text{Oxanilide.}} + 4\ HO;\ \text{and}$$

$$\overbrace{2\,(C_{12}H_5,\ HN)\ C_4O_4}^{\text{Oxanilide.}} = \overbrace{2\,(C_{12}H_4,\ NC_2)}^{\text{Phenylocyanogen.}} + 4\ HO.$$

(1061) The remarkable parallelism in properties of the salts of the organic bases with those of ammonia, will be rendered still more evident by the following additional particulars:—

Many of the vegetable bases may be obtained like ammonia in the anhydrous state: such, for instance, are cinchonia $C_{40}H_{24}N_2O_2$, and strychnia $C_{42}H_{22}N_2O_4$; and the same is the case almost without exception with the aniline class. These anhydrous bases combine directly with the hydracids like ammonia, and do not require any addition of the elements of water; hydrochlorate of cinchonia, for example, consists of ($C_{40}H_{24}N_2O_2$, 2 HCl): but, as is the case also with ammonia, whenever these bases unite with the oxyacids, an equivalent of water is essential to the production of the salt; sulphate of cinchonia, for instance, which contains ($C_{40}H_{24}N_2O_2$, 2 HO, 2 SO_3, 8Aq), loses 8 equivalents of water of crystallization by heat, but the remaining 2 equivalents cannot be expelled without decomposing the salt. The double salts which the organic bases form, also closely resemble the corresponding compounds of ammonia:—for example, with bichloride of platinum they yield yellow crystalline double chlorides of sparing solubility: these compounds are of considerable importance to the chemist, since they furnish him with very accurate means of determining the equivalent number of the vegetable base. Terchloride of gold also forms with them similar compounds, which Hofmann has proposed to employ for the same purpose. Most of the organic bases also furnish nearly insoluble white precipitates when their solutions are mixed with one of corrosive sublimate: and a solution of the mixed sulphates of quinia and persulphate of iron, yields by spontaneous evaporation crystals having the octohedral form of alum (Will). Octohedral crystals are also obtained when a solution of sulphate of conia, which is an analogue of ammonia, is mixed with one of tersulphate of alumina, and left to spontaneous evaporation.

In addition to these compounds there are some others peculiar to this class of bodies. Solutions of salts of the vegetable bases for the most part, when mixed with biniodide of potassium, yield precipitates insoluble in water, but soluble in boiling alcohol, from which they crystallize on cooling. It has been proposed to use these compounds in determining the bases quantitatively for the purposes of analysis. For this purpose the precipitate formed by the biniodide is placed in very dilute sulphuric acid and treated with fragments of zinc; iodide of zinc and protiodide of the base are dissolved; and on the addition of ammonia in excess, the vegetable alkali is precipitated, whilst the zinc is retained in solution. In some cases it is found preferable to throw down both the oxide of zinc and the alkaloid by means of carbonate of ammonia; the precipitate after washing with water is treated with boiling alcohol, which dissolves out the alkali, leaving the oxide of zinc; and on evaporating the alcoholic solution, the alkali is obtained in a state of purity.

Nearly all the organic bases form insoluble curdy precipitates with gallotannic acid: indeed, this acid is one of the most complete precipitants of the vegetable alkalies. These gallotannates, when heated, melt to a resinous mass, and are soluble to some extent in boiling water; they are also dissolved freely by boiling alcohol.

The action of tartaric acid upon the vegetable bases is analogous to that which it exerts on many of the inorganic bases: for instance, the tartrates of iron, of copper, and of some other metals, are not precipitated by the addition of the alkalies to their aqueous solutions; but tartrate of lead is decomposed with separation of the metallic oxide. So it is with many of the organic bases; the tartrates of brucia, of quinia, and of morphia, are not precipitated by an excess of potash or of soda; by converting these organic bases into tartrates and adding an excess of an alkaline solution, they may be separated from strychnia, cinchonia, and narcotine, the [illegible] of which are decomposed in the usual way on the addition [illegible] of ammonia.

[illegible] number of the vegetable bases, when in solution, [illegible] phenomenon of left-handed rotation on a ray of polar[illegible] The artificial bases in general do not possess the power [illegible] polarized ray (Laurent). The left-handed rotation [illegible] becomes right-handed when this base is [illegible] and generally speaking, the effect of the addition of an acid to the base is to reduce its power of rotation, though with quinia the rotatory power is exalted by the addition of an acid.

Artificial Formation of Organic Bases.

(1062) It has already been stated that many organic bases may be prepared by artificial means, several of those derived from the alcohols having been fully described (1027 *et seq.*) All attempts at obtaining those which occur naturally in plants have, however, hitherto been unsuccessful. The following are the principal processes resorted to for the purpose of preparing organic bases artificially:—

1. By destructive distillation of organic bodies containing nitrogen.

2. By distillation of the organic alkalies with hydrate of potash (Gerhardt); and of the cyanic ethers, with hydrate of potash (Wurtz).

3. By combination of ammonia with certain volatile oils, and subsequent moderate heating of the product with solution of potash (Fownes).

4. By reduction of nitrous derivatives of the hydrocarbons by means of sulphuretted hydrogen (Zinin).

5. By substitution of the alcohol radicles for hydrogen in ammonia, by the action of hydrobromic, or hydriodic ethers, upon ammonia (Hofmann).

6. By substitution of the alcohol radicles for hydrogen in phosphuretted, arseniuretted, and antimoniuretted hydrogen, by processes analogous to those last mentioned.

1. *Destructive Distillation of Substances containing Nitrogen.*—This method constitutes the foundation of the manufacture of ammonia, which is always the principal basic substance thus furnished; but since the ammonia is, during this operation, brought into contact with hydrocarbons and with other products of distillation, in their nascent state, the elements of the ammonia react upon these bodies, and produce a small quantity of other bases, homologous with, or derivative from, ammonia. In the preparation of coal-gas, for instance, four, at least, of these compounds come over along with the coal-tar: these are aniline, or kyanol ($C_{12}H_7N$); picoline, a base isomeric with aniline; quinoline, or leukol $C_{18}H_7N$; and pyridine ($C_{10}H_5N$). Stenhouse has shown that when vegetable matters rich in nitrogen, such as the seeds of the leguminosæ and of the cereals, are distilled in a similar way in vessels excluded from the air, in addition to ammonia, large quantities

of volatile oily bases come over, the nature of which varies with that of the compound distilled (*Phil. Trans.*, 1850): and the destructive distillation of bones furnishes an empyreumatic oily liquid, known as *Dippel's oil,* which contains a variety of analogous bases.

2. *Action of Potash on Organic Bodies.*—Sometimes the azotised matters, instead of being distilled alone, are mixed with hydrate of potash, and submitted to the action of heat. In this way aniline is abundantly obtained from indigo, and quinoline from quinia and cinchonia; quinoline is also obtained by similar means, though in smaller proportion from strychnia. Mr. Greville Williams finds that several other volatile bases, including pyridine and several of its homologues, are formed at the same time. Although, therefore, the following equations do not represent the whole of the reaction which occurs under these circumstances, they will serve to point out the simple relation between quinoline and these bases:—

$$\overbrace{C_{40}H_{24}N_2O_2}^{\text{Cinchonia.}} + 6\,HO = \overbrace{2\,(C_{18}H_7N)}^{\text{Quinoline.}} + 4\,CO_2 + H_{16};$$

$$\overbrace{C_{40}H_{24}N_2O_4}^{\text{Quinia.}} + 4\,HO = 2\,(C_{18}H_7N) + 4\,CO_2 + H_{14};$$

$$\overbrace{C_{42}H_{22}N_2O_4}^{\text{Strychnia.}} + 8\,HO = 2\,(C_{18}H_7N) + 6\,CO_2 + H_{16}.$$

In like manner aniline is obtained from isatin:—

$$\overbrace{C_{16}H_5NO_4}^{\text{Isatin.}} + 4\,HO = \overbrace{C_{12}H_7N}^{\text{Aniline.}} + 4\,CO_2 + H_2.$$

The carbonic acid produced during these operations remains in combination with the potash, whilst the hydrogen escapes. It was by distilling the cyanic and cyanuric ethers with hydrate of potash that Wurtz discovered the remarkable bases, methylia, ethylia, and amylia; the reaction being analogous in all these cases (1007):—

$$\overbrace{C_4H_5O,\ C_2NO}^{\text{Cyanic Ether.}} + 2\,(KO,\ HO) = \overbrace{C_4H_5,\ H_2N}^{\text{Ethylia.}} + 2\,\overbrace{(KO,\ CO_2)}^{\text{Carb. Potash.}}.$$

3. Another process consists in combining ammonia with certain of the volatile oils. The compound obtained in this manner in some cases, without further treatment, exhibits the properties of an alkaline base; but in other instances a neutral body is formed, which, when treated with a solution of potash, is converted into an isomeric substance, possessed of basic powers. An example of the first kind occurs when oil of mustard is treated

with ammonia: it thus forms a powerful crystalline base, which, when mixed with acids, at once unites with them, and forms crystallizable salts :—

$$\overbrace{C_8H_5NS_2}^{\text{Oil of Mustard.}} + H_3N \text{ becoming } \overbrace{H_3(C_6H_5)N_2, C_2S_2}^{\text{Thiosinamine.}};$$

or the sulphuretted urea of the allyl series: whilst an instance of the second kind is afforded by bitter almond oil, which, on uniting with ammonia in the proportion of 3 equivalents of the oil with 2 equivalents ammonia, loses 6 equivalents of water, and forms the neutral body, hydrobenzamide :—

$$3\,\overbrace{(C_{14}H_6O_2)}^{\text{Oil of Bitter Almonds.}} + 2\,H_3N = \overbrace{C_{42}H_{18}N_2}^{\text{Hydrobenzamide.}} + 6\,HO.$$

When these crystals of hydrobenzamide are boiled with a solution of caustic potash for some hours, they are gradually converted into benzoline (amarine), an alkaline body insoluble in water, which has the same composition as hydrobenzamide, and forms beautiful salts with acids. In a similar manner Fownes prepared furfurine by acting on the compound of furfurole and ammonia with potash :—

$$\overbrace{3\,C_{10}H_4O_4}^{\text{Furfurole.}} + 2(H_3N) = 2\overbrace{(C_{15}H_6NO_3)}^{\text{Furfuramide.}} + 6\,HO;\ \text{and}\ \overbrace{2(C_{15}H_6NO_3)}^{\text{Furfuramide.}} = \overbrace{(C_{30}H_{12}N_2O_6)}^{\text{Furfurine.}}$$

4. A fourth process for artificially obtaining organic bases is the remarkable one invented by Zinin. Many compounds of carbon and hydrogen, such as benzole, toluole, and naphthalin, when treated with strong nitric acid, lose an equivalent of hydrogen, whilst an equivalent of peroxide of nitrogen takes its place; in this way benzole is converted into nitrobenzole,—

$$\overbrace{C_{12}H_6}^{\text{Benzole.}} + NO_5 = \overbrace{C_{12}H_5NO_4}^{\text{Nitrobenzole.}} + HO;$$

toluole $C_{14}H_8$ into nitrotoluole ($C_{14}H_7NO_4$), and naphthalin ($C_{20}H_8$) in nitronaphthalin ($C_{20}H_7NO_4$). These new compounds are soluble in alcohol; and Zinin found that, after saturating the alcoholic solution with dry ammoniacal gas, and then transmitting sulphuretted hydrogen, the solution, if left to itself, deposited sulphur: water was formed at the same time, whilst the whole of the oxygen was removed from the original compound, and a new substance, possessed of basic characters, was formed in the solution. This substance in many instances might be obtained in crystals on evaporation. Nitrobenzole is thus converted into [illegible] nitrotoluole into toluidine, and nitronaphthalin into naphthalidine thus:—

$$\underbrace{[illegible]NO_4}_{[illegible]} + 6\,HS = \overbrace{C_{12}H_5,\,H_2N}^{\text{Aniline.}} + 4\,HO + 6\,S;$$

$$\underbrace{[illegible]NO_4}_{[illegible]} + 6\,HS = \overbrace{C_{14}H_7,\,H_2N}^{\text{Toluidine.}} + 4\,HO + 6\,S;$$

$$\underbrace{[illegible]NO_4}_{[illegible]} + 6\,HS = \overbrace{C_{20}H_7,\,H_2N}^{\text{Naphthalidine.}} + 4\,HO + 6\,S.$$

In each case the whole of the sulphur is precipitated, whilst 2 [illegible] of hydrogen enter into the combination instead of the 4 [illegible] of oxygen which are removed. The object of adding [illegible] in the first instance is merely to retain the sulphuretted [illegible] in solution, so that the reaction may have time to take [illegible] A large number of new bases have already been formed [illegible] process, and numerous others will, no doubt, shortly be [illegible] Béchamp has shown that by treating nitrobenzole, [illegible] nitrous derivatives of the hydrocarbons, with protacetate [illegible] they are reduced; the protoxide of iron becomes converted [illegible], and is most of it precipitated in the form of a [illegible] of iron, whilst an organic base is formed; and [illegible] is even preferable to Zinin's:—

$$[illegible] + 12\,\overbrace{(FeO,\,\overline{Ac})}^{\text{Protacet. of Iron.}} + 2\,HO = \overbrace{C_{12}H_7N}^{\text{Aniline.}} + \overbrace{6\,Fe_2O_3,\,12\,\overline{Ac}.}^{\text{Basic Peracet. of Iron.}}$$

[illegible] bases thus procured are destitute of oxygen: they [illegible] in their mode of combination with oxyacids, an [illegible] water being essential to the formation of these salts; [illegible], for example, consists of HO, $C_{14}H_9N$, SO_3. [illegible] Wöhler have also formed two bases, termed *thialdine* [illegible] *selenaldine* ($C_{12}H_{13}NSe_4$), in which sulphur and [illegible] constituent elements. They are procured by the [illegible] sulphuretted hydrogen and seleniuretted hydro[illegible] an aqueous solution of 3 equivalents of [illegible] thus in the case of thialdine:—

$$[illegible]\,S = \overbrace{C_{12}H_{13}NS_4}^{\text{Thialdine.}} + 2(H_4NS) + 6\,HO.$$

[illegible] order will be observed in the description [illegible] as, from their important applications, [illegible], or from the mode of their forma[illegible]:—

A. *Artificial Bases.*

1. Bases which do not contain oxygen;
   - *a.* Aniline series $(C_nH_{n-7})H_2N$;
   - *b.* Pyridine series $(C_nH_{n-5})'''N$;
   - *c.* Quinoline series $(C_nH_{n-11})'''N$.
2. Bases obtained by the action of ammonia upon certain essential oils.
3. Bases obtained by the substitution of electro-negative radicles for hydrogen in ammonia.

B. *Natural Bases.*

1. Volatile oily bases destitute of oxygen :—
   Conia ;—Nicotia ;—Sparteia ;—
2. Oxidized bases;
   - *a.* Bases of the cinchonas;
   - *b.* Opium bases;
   - *c.* Alkalies from pepper;
   - *d.* Alkaloids from the strychnos tribe;
   - *e.* Other less known bases;
   - *f.* Caffeine and Theobromine.

A. ARTIFICIAL BASES.

1. *Volatile bases which do not contain oxygen.*

a. Aniline series $(C_nH_{n-7})H_2N$.

(1064) ANILINE, *Kyanol, Phenylamide, Phenylia, Crystalline,* or *Benzidam* ($C_{12}H_7N = C_{12}H_5, H_2, N$). *Sp. gr. of liquid* 1·020, *of vapour* 3·210.—This remarkable base may be prepared from several sources, and by a variety of reactions.

1. It is contained in small quantity among the products of the destructive distillation of coal in the process of gas-making.

2. Nitrobenzole is converted by hydrosulphate of ammonia into aniline and water, whilst sulphur is deposited,

$$C_{12}H_5NO_4 + 6\ HS = C_{12}H_5, H_2N + 4\ HO + 6\ S.$$

A similar reduction takes place under the influence of protacetate of iron, or of a mixture of zinc and hydrochloric acid.

3. It is also furnished by the distillation, with lime, of nitrotoluole, or of its metamerides, salicylamide and anthranilic acid, all of which substances furnish aniline and carbonic acid; thus:—

$$\overbrace{C_{14}H_7NO_4}^{\text{Nitrotoluole.}} = 2\ CO_2 + \overbrace{C_{12}H_5, H_2N.}^{\text{Aniline.}}$$

The product from salicylamide is always accompanied by carbolic acid ($HO, C_{12}H_5O$).

4. One of the methods by which aniline is most abundantly and easily procured consists in mixing finely-powdered indigo with a concentrated solution of hydrate of potash, and submitting it to distillation: the mass swells up greatly, and water, holding ammonia in solution, passes over, accompanied by aniline in the form of a brownish oil. This oil, when re-distilled, furnishes pure aniline, amounting to nearly one-fifth of the weight of the indigo.

This base is a colourless, limpid liquid, of an agreeable vinous odour and burning taste. It is very acrid and poisonous. Aniline remains fluid at —4° F. When dropped upon paper it produces a greasy stain, which, owing to the volatility of the base, speedily disappears; it boils at 360° F. Aniline is a non-conductor of electricity; it refracts light powerfully. When exposed to the air it rapidly absorbs oxygen, and becomes converted into a brown, resinous mass; it is, therefore, necessary to distil it in a current of hydrogen, or of carbonic acid. It is heavier than water, in which it is soluble to a considerable extent; but on saturating the liquid with sulphate of magnesia, the aniline is separated. Aniline has little or no action on test papers; it dissolves in unlimited quantity in alcohol, ether, and wood spirit.

Most of the salts of aniline crystallize readily. They are colourless, but if exposed to the air while moist, they become rose-coloured. If a slip of deal be plunged into a solution of any of these salts, it gradually acquires an intense yellow colour. If an aqueous solution of a salt of aniline be mixed with a solution of chloride of lime, a deep blue colour is produced, which gradually passes into a dirty red. With chromic acid these salts strike a green, a blue, or a black colour, according to the degree of concentration of the solutions. Aniline produces a white precipitate in a solution of corrosive sublimate, and a green crystalline precipitate in one of chloride of copper. Both precipitates contain aniline in combination with the metallic chlorides.

When a solution of hydrochlorate of aniline is mixed with one of nitrite of silver, nitrogen escapes in abundance, whilst carbolic acid is separated in oily drops; owing to the reaction of nitrous acid on aniline:—

$$\overbrace{C_{12}H_7N}^{\text{Aniline.}} + NO_3 = \overbrace{HO, C_{12}H_5O}^{\text{Carbolic Acid.}} + 2\,N + HO.$$

Aniline acts powerfully upon the hydriodic ethers of the different alcohols, in the manner already explained (1027), and yields derived bases, such as ethylaniline [$(C_4H_5, C_{12}H_5, H)N$.] When mixed with the oxychlorides, or with the anhydrides, of the organic acids, aniline yields compounds which correspond with the amides. With acetic oxychloride, for instance, it produces acetanilide, and hydrochlorate of aniline :—

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\ Cl\end{matrix}\right\}}^{\text{Acetic Oxychloride.}} + \overbrace{2(C_{12}H_7N)}^{\text{Aniline.}} = \overbrace{\left.\begin{matrix}C_4\,H_3O_2\\ C_{12}H_5\\ H\end{matrix}\right]}^{\text{Acetanilide.}}N + \overbrace{C_{12}H_7N, HCl}^{\text{Hydrochlorate of Aniline.}}$$

Aniline forms anilidated acids, anilides, dianilides, and aniles. The aniles correspond to the imides of the ammonia group; they contain the elements of 1 equivalent of a dibasic acid and 1 equivalent of aniline, minus 4 equivalents of water. The anilidated acids, which correspond to the amidated acids, are formed from 1 equivalent of a dibasic acid and one of aniline, with the separation of 2 equivalents of water. The compounds enumerated in the following list afford examples of each of these classes of substances :—

Anilides.

Formanilide	$C_{12}H_5$, HN, $C_2\,H\,O_2$
Benzanilide	$C_{12}H_5$, HN, $C_{14}H_5O_2$
Cinnamanilide	$C_{12}H_5$, HN, $C_{18}H_7O_2$

Dianilides.

Oxanilide	$2(C_{12}H_5)$, H_2N_2, C_4O_4
Succinanilide	$2(C_{12}H_5)$, H_2N_2, $C_8H_4O_4$
Suberanilide	$2(C_{12}H_5)$, H_2N_2, $C_{16}H_{12}O_4$

Anilidated Acids.

Sulphanilic acid	HO, $C_{12}H_5$, HN, $S_2\,O_5$
Oxanilic acid	HO, $C_{12}H_5$, HN, $C_4\,O_5$
Succinanilic acid	HO, $C_{12}H_5$, HN, $C_8\,H_4\,O_5$
Camphoranilic acid . . .	HO, $C_{12}H_5$, HN, $C_{20}H_{14}O_5$

Aniles.

Succinanile	$C_{12}H_5N$, $C_8\,H_4\,O_4$
Camphoranile	$C_{12}H_5N$, $C_{20}H_{14}O_4$

Aniline combines directly with cyanogen, and forms a feeble base, termed *cyaniline* ($C_{14}H_7N_2$), which contains the elements of 1 equivalent of aniline and 1 of cyanogen. It is very unstable.

Aniline is remarkable as yielding compounds possessed of basic properties, when portions of the hydrogen are displaced by chlorine or by bromine. These compounds are best obtained by decomposing chlorisatin, dichlorisatin, and trichlorisatin, by means of hydrate of potash (p. 41).

Chloraniline ($C_{12}H_4Cl, H_2N$) is a weaker base than aniline, and is obtained in white, fusible, volatilizable, crystalline needles; its salts have a strong disposition to crystallize; and, like those of aniline, they impart a yellow colour to a slip of deal. *Dichloraniline* ($C_{12}H_5Cl_2N$) is still less basic in its characters than the foregoing substance; and *trichloraniline* ($C_{12}H_4Cl_3N$) is a very volatile crystalline compound, which is entirely devoid of basic properties. The corresponding compounds with bromine, in general properties closely resemble the chlorinated forms of aniline.

The action of chlorine in these cases is very interesting: although the introduction of a single equivalent of this body into the composition of aniline does not destroy the basic character, yet the electro-negative power of chlorine is exhibited in the diminution of the basic energy possessed by the new group, as compared with that of aniline; each successive addition of chlorine weakening the basic property, until it disappears altogether in trichloraniline.

Dr. Hofmann, by whom these bases were discovered, has also succeeded, in conjunction with Dr. Muspratt, in preparing a compound which is termed *nitraniline*, $C_{12}H_4NO_4, H_2N$; this body also forms salts with acids; it contains an equivalent of peroxide of nitrogen in the place of an equivalent of hydrogen. Its basic properties are, however, very feeble.

Hofmann represents aniline as *phenylamine*, or a derivative of ammonia, in which 1 equivalent of hydrogen is displaced by a hydrocarbon $C_{12}H_5$, termed phenyl. Neither phenyl nor its iodide have as yet been isolated; but aniline may be procured by heating hydrated carbolic (phenic) acid in a sealed tube with ammonia:—

$$\overbrace{HO, C_{12}H_5O}^{\text{Phenic Acid.}} + H_3N = 2\,HO + \overbrace{C_{12}H_5, H_2N}^{\text{Aniline.}}$$

(1065) Several other oily bases have been discovered, homologous with aniline; forming part of a series, each member of which differs from the succeeding one in containing one equivalent more of the carbo-hydrogen (C_2H_2). The bases of this class may be obtained from a series of hydrocarbons, of the form (C_nH_{n-6}). These hydrocarbons when treated with nitric acid yield substitution-compounds, in which one equivalent of hydrogen is displaced by one of peroxide of nitrogen (NO_4); and from this nitro-compound, the corresponding base may be obtained by Zinin's process with hydrosulphate of ammonia (1062):—

Hydrocarbon (C_nH_{n-6})		Nitro-substitute ($C_nH_{n-7}NO_4$)		Base ($C_nH_{n-5}N$)	
1. Benzole . .	$C_{12}H_6$	Nitrobenzole .	$C_{12}H_5\ NO_4$	Aniline .	$C_{12}H_7\ N$
2. Toluole . .	$C_{14}H_8$	Nitrotoluole .	$C_{14}H_7\ NO_4$	Toluidine	$C_{14}H_9\ N$
3. Xylole . .	$C_{16}H_{10}$	Nitroxylole . .	$C_{16}H_9\ NO_4$	Xylidine .	$C_{16}H_{11}N$
4. Cumole . .	$C_{18}H_{12}$	Nitrocumole .	$C_{18}H_{11}NO_4$	Cumidine .	$C_{18}H_{13}N$
5. Cymole . .	$C_{20}H_{14}$	Nitrocymole .	$C_{20}H_{13}NO_4$	Cymidine .	$C_{20}H_{15}N$

These bases of the aniline series belong to Hofmann's class of amidogen bases, one equivalent of hydrogen having been displaced by the hydrocarbons, $C_{12}H_5$, $C_{14}H_7$, $C_{16}H_9$, &c.; they still retain two equivalents of hydrogen in a form susceptible of displacement by an equal number of equivalents of the alcohol radicles.

(*b*) *Pyridine Bases* (C_nH_{n-5}) N.

(1066) A series of bases, however, exists, each member of which is metameric with one of those belonging to the aniline group: but in the alkaloids of this class, none of the hydrogen admits of displacement by the alcohol radicles; consequently they must be regarded as belonging to Hofmann's subdivision of nitrile bases. They boil at a lower temperature than the corresponding bases of the aniline series. These compounds have been principally investigated by Anderson, and by Greville Williams. They are furnished by the destructive distillation of a bituminous shale from Dorsetshire; and many of them are also contained in the products of the distillation of bones, and of pit-coal. The following table exhibits the metameric pairs of the aniline and pyridine groups :—

Formulæ.	Aniline series.			Pyridine series.		
		Boiling Point.	Specific Gravity.		Boiling Point.	Specific Gravity.
$C_{10}H_5\ N$	Unknown . .			Pyridine . .	240	
$C_{12}H_7\ N$	Aniline . .	360	1·080	Picoline . .	271	0·955
$C_{14}H_9\ N$	Toluidine . .	388		Lutidine . .	310	
$C_{16}H_{11}N$	Xylidine . .			Collidine . .	356	0·921
$C_{18}H_{13}N$	Cumidine . .	437	0·952	Parvoline . .		
$C_{20}H_{15}N$	Cymidine . .	482		Unknown . .		

The bases of the pyridine series correspond to ammonia in which the three equivalents of hydrogen have been displaced by 1 equivalent of a hydrocarbon, such as ($C_{10}H_5$) or ($C_{12}H_7$); each of these hydrocarbons constitutes a *triatomic group*, corresponding to three equivalents of hydrogen: none of the hydrogen in these hydrocarbons admits of displacement by the alcohol radicles, but Anderson has succeeded in obtaining from the pyridine series some remarkable bases into the composition of which platinum enters. These bases have the closest connexion with those obtained by the action of ammonia on the chlorides of platinum (828). The two platinum bases from pyridine are:—

Platinopyridine $= C_{10}H_3Pt\,N$, or $C_{10}H_3\ 2\ (\frac{1}{2}Pt), N$.
Platosopyridine $= C_{10}H_3Pt_2N$.

In the first of these compounds two equivalents of hydrogen in the hydrocarbon $C_{10}H_5$, have been displaced by *one* equivalent of platinum, which here performs the function assigned by Gerhardt to *platinicum* (pt., eq. 49, see note to 828); whilst in the second compound the two equivalents of hydrogen are displaced by *two* equivalents of platinum, the metal here discharging the function assigned to it by Gerhardt as *platinosum* (Pt., eq. 98). Picoline yields similar compounds with platinum.

When the alkaloids of the pyridine group are treated with iodide of ethyl, compounds are formed belonging to the class of ammonium bases. Anderson has thus obtained iodide of *ethylopyridium* ($C_{10}H_5$, C_4H_5N, I), and iodide of *ethylopicolium* ($C_{12}H_7$, C_4H_5N, I). The hydrated oxides, procured by acting upon these compounds with oxide of silver, are not volatile, and are strongly basic.

Picoline ($C_{12}H_7N$) is the best known base of the series to which it belongs. It is usually extracted from coal tar or from *Dippel's oil* (a product of the destructive distillation of bones), by treating it with hydrochloric acid, and distilling the hydrochloric solution with lime. The volatile bases which pass over are submitted to fractionated distillation, collecting separately those parts which come over at about 270°. Picoline is also obtained when piperine (1082) is distilled with hydrate of potash. Picoline is a colourless, very mobile, oily liquid, of a penetrating odour. It is lighter than water (sp. gr. 0·955), and boils at 271°. It is gradually volatilized by exposure to the air, and it does not, like aniline, become brown under these circumstances. By this fact, as well as by its lower boiling point, and smaller density, picoline is at once distinguished from aniline. Picoline is soluble in water in all proportions. It is not coloured violet by chloride of lime, and is not affected by the addition of chromic acid to its solutions. The salts of picoline crystallize with difficulty, and many of them are deliquescent. The hydrochlorate forms deliquescent prisms.

(*c*) *Quinoline series of Bases*, $(C_nH_{n-11})\,N$.

(1067) In addition to the members of the aniline and pyridine series, coal tar contains a third series of bases of which quinoline is the most important member. Three bases of this class are at present known, viz.:—

		Boiling Point.	Specific Gravity.	
			Liquid.	Vapour.
Quinoline . . .	$C_{18}H_7\,N$	462°	1·081	4·519
Lepidine . . .	$C_{20}H_9\,N$	510°	1·072	5·14
Cryptidine . .	$C_{22}H_{11}N$	525° ?		

They combine with the hydriodic ethers, and form compounds corresponding to ammonium; quinoline, for instance, yields with iodide of ethyl an iodide of *ethyloquinolium* $(C_{18}H_7, C_4H_5, N, I)$. These compounds, therefore, like those of the pyridine group, belong to the class of nitrile bases.

Quinoline or *Leukol* $(C_{18}H_7N)$, *Sp. gr. of liquid* 1·081, *of vapour* 4·519.—This alkali is readily obtained by decomposing cinchonia with hydrate of potash: the resinous mass which is separated under the name of quinoidine, during the preparation of the salts of quinia, also yields it by similar treatment. Fragments of the hydrate of potash are placed in a tubulated retort, moistened with a few drops of water, and powdered cinchonia is added in small quantities at a time; on applying heat, the new base passes over, accompanied by free hydrogen; if the product be redistilled, an aqueous solution of ammonia with portions of the base pass over first, and the latter portions consist of nearly pure quinoline, which may be rendered anhydrous by a second rectification, after it has stood for some days upon chloride of calcium.

Quinoline is a colourless oil of high refracting power; it has a disagreeable penetrating odour, and a bitter acrid taste. It remains liquid at $-4°$. At 462° it boils, emitting a vapour which burns with a smoky flame. When exposed to the air it slowly becomes converted into a resinous mass. If dropped upon paper it leaves a greasy stain, which quickly disappears. It is dissolved sparingly by water, but it is soluble in all proportions in alcohol, ether, wood spirit, and bisulphide of carbon, as well as in the fixed and essential oils. The nitrate, the oxalate, and the bichromate of quinoline, crystallize with facility; many double salts of quinoline, such as those which it forms with platinum, gold, palladium, and cadmium, may be obtained in beautiful crystals. The platinum salt is nearly insoluble in water.

A fourth series of bases, provisionally termed *pyrrol bases* by Anderson, is contained in Dippel's oil: they have been but incompletely examined, but are characterized by yielding a red resinous matter when decomposed. Anderson regards them as bases of the pyridine series, coupled with the body which occasions this red colour.

2. *Bases produced by the action of Ammonia on Essential Oils.*

(1068) During the process of obtaining formic acid by distilling bran or oatmeal with peroxide of manganese and dilute sulphuric acid, a small quantity of an essential oil distils over, which may be purified by redistillation. To this body the name of *furfurole* ($C_{10}H_4O_4$) has been given. When pure it is colourless, but it quickly becomes brown by exposure to the air. It has a fragrant odour, somewhat resembling that of bitter almonds. It has a sp. gr. in the liquid form of 1·168, and in vapour of 3·34. Furfurole boils at 323°; it is dissolved by cold sulphuric acid, forming a beautiful purple liquid, from which on dilution with water the oil is separated unchanged. If mixed with solution of ammonia in the cold, furfurole is gradually converted into a solid yellowish-white insoluble mass, 3 equivalents of furfurole reacting upon 2 equivalents of ammonia, while 6 of water are separated; $3\,(C_{10}H_4O_4) + 2\,H_3N = 2\,(C_{15}H_6O_6) + 6\,HO$. This new compound belongs to the class of hydramides (1050), it has been termed *furfuramide.* Acids immediately decompose it, a salt of ammonia is formed, and the oil is set at liberty. When boiled with potash, however, no ammonia is evolved; the substance is completely dissolved, and the solution on cooling deposits long silky needles of a powerfully alkaline base which is isomeric with furfuramide.

Furfuria or *furfurine* ($C_{30}H_{12}N_2O_6$), as this base has been named, is inodorous and sparingly soluble in water; alcohol and ether dissolve it freely. It melts below 212° to an oily-looking liquid. It is dissolved by dilute acids, and completely neutralizes them; on adding ammonia to these solutions, the alkaloid is precipitated unchanged. Its salts have a bitter taste; they have been used medicinally, with success, as substitutes for those of quinia (Gregory).

Benzoline or *amarine* ($C_{42}H_{18}N_2$).—When a solution of ammonia is allowed to remain for some days in contact with pure hydride of benzoyl (essential oil of bitter almonds), a reaction occurs analogous to the foregoing one with furfurole; the mixture gradually becomes converted into a crystalline mass of hydrobenzamide; this substance is soluble in alcohol, but insoluble in water. If boiled with a solution of potash it assumes the appearance of a resin, and becomes changed into *benzoline*, which is a base isomeric with hydrobenzamide. The same change occurs if hydrobenzamide be simply heated for some time to a temperature between 250° and 265°. If the mass which is obtained by either of these methods be treated with boiling alcohol, it is dissolved, and the solution on cooling deposits the base in brilliant transparent four-sided prisms, which are fusible below 212°. Benzoline is nearly insoluble in water, but it is readily dissolved by both alcohol and ether. Its salts, with the exception of the acetate, are sparingly soluble, and have an intensely bitter taste. When benzoline is submitted to destructive distillation, a new base, *pyrobenzoline*, or *lophine* ($C_{42}H_{17}N_2$), is formed, amongst other products.

3. *Bases containing Electro-negative Radicles of the form* (C_nH_{n-1}).

(1069) It will be unnecessary to allude further to the fifth and sixth methods (p. 255) of the formation of bases by the substitution of the alcohol radicles for the hydrogen in ammonia and phosphuretted hydrogen, since this part of the subject has been already fully examined (1027, *et seq.*); but it is an interesting circumstance, that bases may also be obtained which contain the electro-negative hydrocarbons (C_nH_{n-1}) in the place of hydrogen. For example, Natanson (Liebig's *Annalen*, xcii. 48, and xcviii. 291), has succeeded in preparing a substance which he terms *acetylamine*, (acetylia); this body is a derivative from ammonia, but it contains an equivalent of Liebig's electro-negative radicle acetyl (C_4H_3), in the place of one equivalent of hydrogen; acetylia being (C_4H_3, $H_2N = C_4H_5N$); the same chemist has likewise isolated a compound corresponding in composition to hydrated oxide of ammonium; this new base may be termed *hydrated oxide of acetylium*, C_4H_3, H_3N, O.HO.

Acetylium.—When Dutch liquid (C_4H_3Cl, HCl) is heated for some hours to a temperature of 300° in a sealed tube, with about 5 times its bulk of a concentrated solution of ammonia, it is completely decomposed; a yellow liquid is formed, and crystals of chloride of ammonium are deposited in abundance: if these be separated by filtration through muslin, and the mother liquor be treated with oxide of silver, it yields a decidedly alkaline solution, which absorbs carbonic acid from the air. The new base thus obtained is not volatile, its salts have a feebly acid reaction, and do not crystallize. If its chloride be mixed with a solution of bichloride of platinum it yields a wax-like mass, which has the composition of the double chloride of platinum and acetylium (C_4H_3, H_3NCl, $Pt\ Cl_2$). Chloride of acetylium, if slightly acidulated with sulphuric acid and mixed with nitrite of silver, furnishes aldehyd in abundance:—

$$\overbrace{C_4H_3,\ H_3NCl}^{\text{Chloride of Acetylium.}} + AgO,\ NO_3 = \overbrace{C_4H_3O,\ HO}^{\text{Aldehyd.}} + 2\ N + 2\ HO + AgCl.$$

This reaction corresponds to that of nitrous acid on ethylia, by which alcohol is reproduced whilst nitrogen and water are liberated.

The formation of this compound oxide of ammonium, in which three out of the four equivalents of hydrogen in ammonium are retained, is certainly a very remarkable circumstance, and it affords one of the strongest arguments in favour of the ammonium theory. It also strengthens the probability that olefiant gas is a hydride of acetyl (C_4H_3, H). It may be remarked that hydrated oxide of acetylium is metameric with aldehyd-ammonia, although so different from it in properties:—

$$\overbrace{C_4H_3,\ H_3NO,\ HO}^{\text{Hydrated Oxide of Acetylium.}} = \overbrace{C_4H_4O_2,\ NH_3.}^{\text{Aldehyd-ammonia.*}}$$

Acetylia (C_4H_3, H_2N), *Sp. gr. of liquid* 0·975; *of vapour* 1·522. —If an alcoholic solution of the hydrated oxide of acetylium be distilled to dryness in a retort, and the temperature be then raised to about 300°, water again begins to escape, and at a temperature of 428° yellowish oily drops of acetylia pass over. This body has a peculiar persistent odour, which is ammoniacal, and at the same time recalls that of aldehyd. It boils at about 425°, and does not become solid at $-13°$. It is inflammable, and burns with a bluish white flame. It is insoluble in ether, but freely soluble both in water and in alcohol. Sodium exerts no action upon acetylia at ordinary temperatures. Dry reddened litmus paper does not become blue even when immersed in acetylia; but if the base be treated with acids it forms salts which are identical with those of oxide of acetylium. If potash be added to a solution of these salts, the liquid does not emit the odour of acetylia, but exhibits the properties of a solution of hydrated oxide of acetylium. An aqueous solution of acetylia produces in a solution of the salts of zinc, a white precipitate which is soluble in excess of the base. With salts of copper it gives a pale yellow precipitate, which is partially soluble if acetylia be added in excess, forming a bright blue liquid. It occasions a white precipitate in solutions of the salts of silver, but the precipitate is readily dissolved by an excess of the base, and if the solution be gently warmed, a mirror-like coating of reduced silver is formed on the sides of the vessel.

It is remarkable that the oxide of acetylium should be so permanent a body as to require a temperature of 300° for its decomposition, although the corresponding compound of ammonium undergoes decomposition as soon as it is formed at ordinary temperatures. Acetylia corresponds exactly with ammonia, and like it does not form salts until it has assimilated an equivalent of water.

Formyl also enters into the composition of a base (C_2H, H_2N), termed *formylia*, which is homologous with acetylia.

If acetylia be treated with iodide of ethyl, *ethyl-acetylia* is obtained, a base which is represented by the formula C_4H_3, C_4H_5, HN. *Phenylacetylia* ($C_4H_3, C_{12}H_5, HN$) is procured by treating Dutch liquid with aniline instead of with ammonia:—

$$\overbrace{C_4H_4Cl_2}^{\text{Dutch liquid.}} + 2\,\overbrace{(C_{12}H_7N)}^{\text{Aniline.}} = \overbrace{C_{12}H_7N, HCl}^{\text{Hydrochlorate of aniline.}} + \overbrace{C_4H_3. C_{12}H_5, HN, HCl.}^{\text{Hydrochlorate of phenylacetylia.}}$$

Acetylia also produces compounds corresponding to the amides. Thus, when butyric ether is mixed with an alcoholic solution of acetylia, crystals of *butyric acetylamide* $\left.\begin{matrix}C_8H_7O_2\\C_4H_3\\H\end{matrix}\right\}N$, are formed.

B. NATURAL BASES.

1. *Volatile oily bases destitute of oxygen.*

(1070) CONIA ($C_{16}H_{15}N$) is the active principle of the hemlock (*Conium maculatum*); it pervades the whole plant, but is most easily obtained from the seeds. As it is volatile, it is obtained by distilling hemlock seeds with water which contains a small quantity of potash in solution; conia then passes over with the water in the form of a yellowish oil. When purified by redistillation, conia is a colourless, transparent, volatile, oily liquid of sp. gr. 0·89. It has a powerful, penetrating, most unpleasant and oppressive odour, like that of the fresh plant. A drop of it, when placed upon paper, produces a temporary greasy stain. It is soluble to some extent in water, but is much less so in hot than in cold water; ether and alcohol dissolve it freely. It boils at 340° (Blyth), producing an inflammable vapour.

According to Kekulé and Planta there are two homologous varieties of conia contained in the plant; viz. *conia* ($C_{16}H_{15}N$), and *methylconia* ($C_{18}H_{17}N$): when either of these bases was acted upon by iodide of ethyl or of methyl, new substitution bases were obtained, furnishing the following series of compounds:—

Conia . . . . . $C_{16}H_{15}N = H\ (C_{16}H_{14})N$
Methyl-conia . . . $C_{18}H_{17}N = C_2H_3\ (C_{16}H_{14})N$
Ethyl-conia . . . $C_{20}H_{19}N = C_4H_5\ (C_{16}H_{14})N$
Hydrated oxide of ethyl-methyl-conium $C_{22}H_{22}NO, HO = C_4H_5, C_2H_3\ (C_{16}H_{14})O, HO.$

These experiments show that conia must be regarded as an imide base from which ammonium bases may be procured.

When normal conia ($C_{16}H_{15}N$) is exposed to the air, it rapidly absorbs oxygen; first becoming brown, and ultimately nearly solid. Conia has a powerful alkaline reaction; it neutralizes the acids perfectly, and precipitates many of the metallic oxides from their salts; in all its forms it is a most dangerous poison. Its salts crystallize with difficulty; if their solutions are evaporated in the air, they are decomposed, becoming red or violet in colour, and ultimately assuming a dark green or a blue tint. Strong sulphuric acid causes its compounds to become, first, of a purple red colour, and then of an olive green. With nitric acid it gives a blood red colour, fading into orange; butyric acid is one of the products of this reaction. Conia unites with cyanic ether, and forms immediately a compound urea:—

$$\overbrace{C_4H_5O, C_2NO}^{\text{Cyanic Ether.}} + \overbrace{C_{16}H_{15}N}^{\text{Conia.}} = \overbrace{C_{22}H_{20}N_2O_2}^{\text{Ethylconylurea.}}, \quad \text{or} \quad \left.\begin{matrix} 2(C_2O_2) \\ 2(C_8H_7) \\ C_4H_5 \\ H \end{matrix}\right\} N_2$$

(1070 *bis*) SPARTEIA ($C_{16}H_{13}N$).—In the *Spartium scoparium*, or common broom, Stenhouse discovered an oily base, to which he gave the name of *sparteine*. It possesses narcotic properties, is considerably heavier than water, and has a faint odour recalling that of aniline; when pure it is colourless, but it gradually becomes brown by exposure to the air. It boils at 550°. With bichloride of platinum, and with corrosive sublimate, it forms double chlorides, which crystallize readily; but its other salts are obtained in crystals with difficulty. The hydrochlorate appears to undergo partial decomposition if boiled with excess of hydrochloric acid, and it emits an odour like that of mice. Both the base and its salts have an extremely bitter taste. Sparteine contains 2 equivalents of hydrogen less than conia. The broom plant also contains a neutral, yellow, crystallizable principle, termed *scoparin* ($C_{20}H_{11}O_{10}$), to which its diuretic properties appear to be owing.

(1071) NICOTIA, or *Nicotine* ($C_{10}H_7N$); *comb. vol.* 2; *Sp. gr. of liquid* 1.027 at 66°; *of vapour* 5·607.—This is another remarkable volatile base, which is destitute of oxygen. It is the active principle of the tobacco plant (*Nicotiana tabacum*), in which it occurs in combination with malic and citric acids. It is also contained in the smoke of the burning leaves. Nicotia is a limpid, colourless, oily liquid, with an extremely irritating and powerful odour of tobacco. It is very inflammable, and burns with a smoky flame. It may be distilled readily along with the vapours of water, or in a current of hydrogen gas; though its boiling point is as high as 480°. If exposed to the air it absorbs oxygen, becoming brown, and ultimately solid. Nicotia is very soluble in water, and in the fixed oils; it is also soluble in all proportions in alcohol and ether. Ether, if agitated with the aqueous solution, extracts the whole of the alkali; and the ethereal solution rises to the surface when the two liquids are left at rest. Nicotia is extremely poisonous, a single drop of it being sufficient to kill a large dog. It exerts left-handed rotation on a polarized ray. Its solution forms a white precipitate in a solution of corrosive sublimate, as well as in one of acetate of lead, and of both the chlorides of tin. The white precipitate which it occasions in solutions of the salts of zinc is soluble in excess of nicotia. Salts of copper, with an excess of nicotia yield a blue solution, like that which they produce when supersaturated with ammonia.

Chlorine acts powerfully upon nicotia, producing with it a blood red liquid. Iodine forms with the alkali a crystallized combination ($2\ C_{10}H_7N,I_3$) which has a ruby red colour: potash decomposes this compound, liberating pure nicotia. The salts of nicotia crystallize with difficulty: they are neutral, and are very soluble in water and alcohol, but insoluble in ether, with the exception of the acetate. The proportion of this alkali varies greatly in different samples of tobacco. French tobacco contains 7 or 8 per cent.; Virginia, 6 or 7 per cent.; and Maryland and Havannah, not more than 2 per cent., which is the proportion in ordinary snuff.

Nicotia appears to belong to the class of nitrile bases; the hydrocarbon ($C_{10}H_7$) which it contains, being equivalent in function to the three equivalents of hydrogen in ammonia. This base enters into direct combination with iodide of ethyl, and with iodide of methyl; forming compounds which correspond to the iodide of tetrethylium; and when these compounds are treated with recently precipitated oxide of silver, they yield a powerfully alkaline, inodorous, very bitter substance, which rapidly attracts carbonic acid from the air; for example:—

$$\overbrace{C_{10}H_7, C_4H_5, N}^{\text{Iodide of Ethylnicotium.}}I + AgO, HO = C_{10}\overbrace{H_7, C_4H_5NO, H}^{\text{Hydrated Oxide of Ethylnicotium.}}O + AgI$$

(Kekulé and Planta, Liebig's *Annal.*, lxxxvii. 1).

The best process for preparing nicotia is that employed by Schlœsing. He evaporates the aqueous infusion of tobacco leaves to the consistence of syrup, and adds twice its volume of alcohol of sp. gr. 0·837. The liquid is thus separated into two layers; the upper one, which contains the salts of nicotia, is decanted, concentrated by evaporation, mixed with a solution of potash, and briskly agitated with ether. The ether dissolves the liberated nicotia and some fatty matters, and rises with them to the surface when the mixture is left at rest. In order to purify the alkali, powdered oxalic acid is added by degrees to the decanted ethereal solution. The oxalate of nicotia, being insoluble in ether, forms a dense syrupy layer at the bottom of the vessel. It is washed two or three times with pure ether; and the nicotia is separated by the addition of a fresh quantity of solution of potash and ether. The ethereal solution is decanted into a retort, provided with the means of transmitting a current of dry hydrogen through it; the ether is then driven off, and the residue exposed for twenty-four hours to a temperature of 284°, in order to expel the last traces of ammonia and ether; after which the temperature is raised to 356°, when the nicotia distils over, in a state of purity.

(1072) *Preparation of Snuff.*—A full account of this operation, as performed at the Imperial tobacco works in Paris, is given by Pelouze and Fremy (*Traité de Chimie*, 2nd edition, IV. 437). The following is an outline of the steps of the manufacture:—The stronger kinds of tobacco are those which are preferred for the preparation of snuff. The leaves are spread out in thin layers upon a stone pavement, and moistened with about a fifth of their weight of chloride of sodium and water (sp. gr. 1·089). The moistened leaves are next cut into blocks, and are then piled up in large rectangular heaps, in quantities of forty or fifty tons. These masses gradually enter into fermentation, and the temperature rises sometimes as high as 170°, but usually it does not exceed 140°. If the temperature be allowed to rise too high, some parts of the mass become black, as though they had been charred. Spring and autumn are the seasons most favourable for the commencement of this operation, which requires careful watching, to prevent the development of heat from becoming excessive. In about five or six months the temperature becomes stationary, or begins to decline; the heaps are then opened out, and the fermented mass is submitted to grinding. The pale brown, and comparatively, dry powder thus obtained, is next mixed with about four-tenths of its weight of the solution of chloride of sodium, and is passed through a sieve, to ensure a uniform moistening of the mass; after which it is packed in large oaken chests, capable of containing from twenty-five to fifty tons of the material. Here the snuff remains for nine or ten months, and undergoes a second fermentation, in the course of which the temperature in the centre of the mass rises to 120° or 130°. During this process the snuff acquires its well-known dark colour, and the aroma is developed. The mass is, however, still far from uniform in quality, throughout; it is, therefore, transferred to a second chest, in which operation all the different parts of the heap are thoroughly mixed together; after the lapse of two months, it is a second time turned over, and, sometimes, a third transfer is deemed requisite. When considered ripe, the contents of the various chests are mixed in a large room, capable of containing 350 tons of snuff. Here it is left for about six weeks, to render the entire mass uniform in quality; and finally it is sifted into barrels for the market. The whole process of manufacture thus occupies from eighteen to twenty months. During the fermentation, about two-thirds of the nicotia is destroyed. A small portion of this base appears to exist in snuff, in the uncombined form; but, the greater part of the portion still remaining, is left in the form of acetate: a certain amount of acetic acid having become developed during the fermentation. A portion of the decomposed nicotia becomes converted into carbonate of ammonia, which is partially retained by the snuff; and the gradual volatilization of this salt appears to favour the conversion of nicotia into vapour, and thus to occasion the pungent odour for which snuff is valued. The proportion of citric and malic acids becomes diminished during the fermentation; so that ordinary snuff has an alkaline reaction. A certain quantity of a peculiar essential oil appears also to be developed during the operation; and to the variable proportion of this oil, much of the difference in the flavour of the different varieties of snuff is owing. The quantity of nitrate of potash which fresh tobacco contains, passes over, unaltered, into the snuff.

It may be remarked, that tobacco is one of the most exhausting crops which can be grown upon any soil, since it carries off an enormous amount of mineral constituents (the proportion of ash amounting to not less than 21 per cent. of the dry leaf). Among these constituents, nitric acid is found in quantity often exceeding 2 per cent. of the dry leaf; whilst the salts of potash amount to more than a third of the saline residue.

It is probable that the active principle of henbane or *Hyoscyamus niger*, is a volatile base, analogous to nicotia; since a portion of it comes over when the plant is distilled with a solution of potash. Much of the alkaloid, however, is decomposed in this operation: its composition has not been determined.

2. *Bases which contain oxygen.*

(*a*) *Alkaloids of the Cinchonas.*

(1073) In the bark of the different varieties of *Cinchona*, several well characterized and important bases occur. They are all closely related to each other in composition, and are found, in combination with kinic and kinotannic acids, in the bark. The most abundant of these bodies are *cinchonia* and *quinia*, each of which is accompanied by, or is convertible into, two isomeric bases, termed respectively, *cinchonidine* and *cinchonicine*, and *quinidine* and *quinicine*. Besides these, a base termed *aricine*, or *cinchovatine*, has been found in the bark of the *cinchona ovata*. Until recently it was supposed that the formula of cinchonia was $C_{20}H_{12}NO$, and that of quinia $C_{20}H_{12}NO_2$; but the researches of Strecker appear to indicate that these formulæ must be doubled. Both cinchonia, and quinia form two classes of salts; one class of which has been regarded, until quite recently, as being basic, whilst the other was supposed to be neutral: the common medicinal sulphate of quinia, for example, was viewed as the basic sulphate. If the formula of the base be doubled, however, this salt will be neutral, whilst that formerly regarded as neutral, must be an acid salt. The salts which these bases form with the smaller proportion of acid are very sparingly soluble in water, but are readily dissolved on the addition of any free acid.

Quinia and cinchonia, as well as cinchonidine, appear to belong to Hofmann's class of nitrile bases; since, when treated with iodide of methyl, or with iodide of ethyl, they yield bases of the ammonium type. Hydrated oxide of *ethyloquinium* 2 ($C_{20}H_{12}NO_2$), C_4H_5O, HO is a powerful base, which attracts carbonic acid from the air: the iodide of *methyloquinium* consists of 2 ($C_{20}H_{12}NO_2$), C_2H_3I. The iodides of the corresponding derivatives of cinchonia and cinchonidine, each consist of 2 ($C_{20}H_{12}NO$), C_2H_3I. Induced by these and other circumstances, Strecker doubles the old formula of these alkaloids, representing quinia as $C_{40}H_{24}N_2O_4$.

Cinchonia and quinia, with their isomerides, are decomposed when distilled with hydrate of potash. Several volatile bases are formed, amongst which quinoline (1067) is the most abundant; and formiate of potash is left in the retort.

Cinchonia and its isomeric congeners, are most abundant in the pale Peruvian Bark. Quinia, and its isomeric companions, occur most abundantly in the yellow Bark, or *cinchona cordifolia*; whilst the red Bark contains both classes of alkaloids.

Quinia, from its febrifuge and antiperiodic powers, is the most highly esteemed of these alkaloids for medicinal purposes; though it appears that quinidine possesses similar therapeutic virtues to a nearly equal extent.

(1074) 1. CINCHONIA ($C_{40}H_{24}N_2O_2$) crystallizes in large quadrilateral prisms, which are anhydrous; they are less soluble in alcohol than quinia, and are insoluble in ether. Cinchonia is dissolved by solutions of the alkalies, and alkaline bicarbonates. At 329° F. it fuses to a colourless liquid, which becomes a crystalline mass on cooling; when heated further it is partially volatilized; but a portion, at the same time, undergoes decomposition. It may be sublimed, readily, in an atmosphere of hydrogen. Its salts are intensely bitter; they are precipitated by infusion of galls, as well as by solutions of the oxalates, tartrates, and gallates. Two equivalents of the hydrogen in cinchonia may be displaced by chlorine, and by bromine: the new compounds thus obtained retain their basic characters.

Sulphate of cinchonia (HO ($C_{40}H_{24}N_2O_2$), SO_3, 2 Aq) crystallizes in irregular prisms, which melt, like wax, at a little beyond 212°; when gently heated, it emits a phosphorescent light. If it be first moistened with water acidulated with sulphuric acid, it may be kept in a fused condition for some hours; during which time it gradually passes into the sulphate of cinchonicine (Pasteur). If heated more strongly it is converted into a resinous mass, of a beautiful red colour. The *Bisulphate* (2 HO, $C_{40}H_{24}N_2O_2$, 2 SO_3, 6 Aq) is very soluble both in water and in alcohol; it crystallizes from a hot solution, in large, well-defined, rhombic octohedra. When cinchonia is dissolved in sulphuric acid, and heated with peroxide of lead, it produces a red-coloured compound; when mixed with chlorine water and afterwards with ammonia, no green tint is produced, as occurs when quinia is similarly treated. Its salts are generally more soluble both in alcohol and in water, than those of quinia.

2. *Cinchonidine* ($C_{40}H_{24}N_2O_2$).—This alkali, which is isomeric with cinchonia, occurs naturally in certain varieties of cinchona bark; and may be obtained by the spontaneous evaporation of its alcoholic solution, in hard, brilliant, striated, rhomboidal prisms, which are anhydrous, and insoluble in ether. Its solution in absolute alcohol produces left-handed rotation upon a polarized ray; whilst cinchonia produces rotation to the right. Cinchonidine fuses at 347°, and, at a higher temperature, is decomposed, emitting an odour of oil of bitter almonds.

When the solutions of the salts of this base are mixed with the caustic alkalies, or with the carbonates or bicarbonates of these bases, they give a white precipitate of cinchonidine, which gradually becomes crystalline. Phosphate of soda, corrosive sublimate, nitrate of silver, and sulphocyanide of ammonium, also give white precipitates in solutions of salts of cinchonidine. At a high temperature, the salts of cinchonidine pass into those of cinchonicine. The *Sulphate* ($C_{40}H_{24}N_2O_2,HO, SO_3$) crystallizes in stellate groups of silky needles, the solution of which is neutral to test papers. The hydrochlorate crystallizes in large, brilliant, rhomboidal prisms, soluble in about twenty-seven parts of water.

3. *Cinchonicine* is a third base, which has the same composition as the two foregoing ones. It is precipitated from its salts in the form of a resinous mass, which is freely soluble in alcohol. This solution causes right-handed rotation of a ray of polarized light. Cinchonicine is best prepared by the action of heat upon the sulphate of cinchonine, in the manner already mentioned.

(1075) 4. QUINIA ($C_{40}H_{24}N_2O_4$, 6 Aq) is most abundant in the yellow bark (*cinchona cordifolia*), in which it occurs mixed with cinchonia, and combined with kinic and kinotannic acids. The quantity of the alkaloids varies in different specimens of bark, but the two together generally amount to 3·5 or 4 per cent. In order to extract the bases, the pulverized bark is boiled with 8 or 10 parts of water acidulated with 1 part of oil of vitriol, or with 2 parts of hydrochloric acid. The liquid is strained through a cloth, and the residue is boiled twice with water less strongly acidulated. When the strained liquors are cold, milk of lime, or carbonate of soda is added in slight excess, the precipitate is submitted to pressure, and then treated with hot alcohol. If the proportion of cinchonine be considerable, it crystallizes as the liquid cools; and a fresh quantity is obtained by distilling off one half of the alcohol from the residue, whilst the quinia remains in solution; the liquid is then neutralized with sulphuric acid. The separation of the two bases is afterwards completed by crystallizing the mixed sulphates from a slightly acid solution; the sulphate of quinia being much the less soluble of the two, crystallizes first. The alkaloid is then thrown down from the sulphate by adding ammonia. Cinchonia and cinchonidine may also be separated from quinia by means of ether, which dissolves the quinia, and leaves the cinchonia and cinchonidine.

Quinia may be obtained in crystals, though with some difficulty, by allowing its alcoholic solution to evaporate spontaneously in a cool place: silky needles are thus formed; they are dissolved much more readily by cold alcohol than the crystals of cinchonia. Quinia requires about 350 parts of water for its solution. By a heat of 240°, 6 equivalents of water are expelled, and at a little above this point the alkali fuses into a resinoid mass, which may be distilled in great part without decomposition. Quinia is also soluble both in the essential and in the fixed oils.

Quinia yields crystallizable salts; but when these salts are exposed in solution to a strong light, or when they are treated with an excess of acid, they pass into a resinoid amorphous condition, and constitute the substance met with in the shops as *quinoidine,* which is also contained abundantly in the mother liquors from which the salts of quinia have been crystallized. The employment of an excess of acid in extracting the alkali from the bark should be avoided, since it appears to increase the formation of this uncrystallizable substance. Quinoidine is a mixture of several basic compounds, among which are all the alkaloids of the cinchona bark. In some instances as much as 50 or 60 per cent. of crystallized quinidine have been extracted from it by treatment with ether. Pasteur considers that the production of quinoidine might be greatly diminished if more care were taken in drying the bark upon the spot where it is collected. Exposure to the sun's rays should be avoided, for it is found that direct sunlight has a remarkable influence in producing the change of the crystallizable alkaloids into the uncrystallizable form.

The salts of quinia have an intensely bitter taste; they give abundant precipitates with tincture of galls, nitrate of red oxide of mercury, and nitrate of silver, also with gallic, tartaric, and oxalic acids, and their salts. If quinia be suspended in water, and chlorine be transmitted through the liquid, the alkali is dissolved, and the solution passes successively through various shades of rose, violet, and dark red. The following reaction is regarded as characteristic of quinia: when freshly prepared chlorine water is poured into a solution of one of the salts of this alkali, and then a few drops of ammonia are added, a green colour is produced.

The presence of cinchonia in the salts of quinia may be detected in several ways; one of the best is that proposed by Liebig: 10 grains of sulphate, or other salt of quinia suspected to be impure, are placed in a test tube with 2 drachms of washed ether, and 20 drops of a solution of caustic ammonia are added. The mixture is briskly shaken, and on standing it separates into two layers, the upper one consisting of an ethereal solution of quinia, the lower one of an aqueous solution of sulphate of ammonia; the cinchonia being insoluble in either liquid floats upon the surface of the watery layer. The fraudulent admixture of salicin with the salts of quinia is detected by the addition of a few drops of oil of vitriol to the salt; if salicin be present it gives a red colour to the mixture.

The ***sulphate of quinia***, usually called the ***disulphate***, ($HO, C_{40}H_{24}N_2O_4, SO_3 + 7\ Aq$), is the salt employed in medicine: it crystallizes in snow-white, very light, bulky, efflorescent needles, which are sparingly soluble in water, but abundantly so in dilute sulphuric acid and in alcohol. The acidulated solution shows the phenomenon of fluorescence (104) in a striking manner. Sulphate of quinia fuses easily on the application of heat, and emits a phosphorescent light. An *acid sulphate* ($C_{40}H_{24}N_2O_4, 2HO, 2SO_3, 14Aq$), may be obtained by dissolving the foregoing salt in sulphuric acid and concentrating the liquid; it crystallizes in small needles, which are freely soluble in water, and in alcohol.

A remarkable compound of iodine and sulphate of quinia ($C_{40}H_{24}N_2O_4I_2, 2\ HO, 2\ SO_3 + 10\ Aq$), has been described by Dr. Herapath. It may be obtained by dissolving the bisulphate of quinia in concentrated acetic acid, and adding to the heated liquid, an alcoholic solution of iodine, drop by drop. After standing for a few hours, the salt is deposited in large flat rectangular plates, which when seen by reflected light are of a brilliant green colour, with a metallic lustre, like the wing cases of the blistering beetle. When viewed by transmitted light they appear of a pale olive tint, but the light so transmitted is perfectly polarized; so that if a second plate cross the first at right angles, the whole of the light is as completely arrested by the overlapping portions, as it would be by two overlapping plates of tourmaline, the axes of which cross each other at right angles (113). Quinia passes unchanged into the urine, and may readily be detected in this excretion from patients to whom it has been freely administered.

5. *Quinidine* ($C_{40}H_{24}N_2O_4$, 4 Aq), is a base isomeric with quinia. It is extracted from quinoidine by treatment with ether. The ethereal solution if left to spontaneous evaporation crystallizes with facility, in long rhombic efflorescent prisms. The solution of quinidine in absolute alcohol produces right-handed rotation of a polarized ray (Pasteur), whilst a similar solution of quinine produces rotation to the left (Bouchardat). Quinidine is much less soluble in water than quinia, for it requires about 1500 parts of cold water for solution; but it is much more soluble than quinia in ether. When heated, it loses its water of crystallization, and it fuses at 320°. The acid sulphate of quinidine is much less soluble than the corresponding salt of quinia; whilst the oxalate is freely soluble in water, and may thus be separated from the oxalate of quinia, which is sparingly soluble. Chlorine and ammonia produce a green coloration with the salts of quinidine, similar to that which they occasion with those of quinia.

6. *Quinicine* is produced by the action of heat upon the salts of quinia and quinidine. It is precipitated by alkalies in the form of a fluid resinous mass, which combines readily with acids, and forms bitter uncrystallizable salts, endued with febrifuge properties. These salts are metameric with those of quinine. Quinicine is freely soluble in alcohol: the solution produces right-handed rotation of a ray of polarized light.

The relation of the cinchona alkalies to polarized light is remarkable, and may thus be exhibited:—

Quinia produces a powerful left-handed rotation.
Quinidine „ a powerful right-handed „
Quinicine „ a feeble right-handed „
Cinchonia „ a powerful right-handed „
Cinchonidine „ a powerful left-handed „
Cinchonicine „ a feeble right-handed „

Pasteur considers that quinia and cinchonidine each contain two active groups, one of which produces strong left-handed rotation, the other produces a feeble right-handed rotation. He also regards quinidine and cinchonia as each consisting of two groups; one of which exerts a powerful right-handed rotation, and the other a feeble left-handed rotation; and he supposes that in each of these bases, by the agency of heat, the more powerful group is rendered inert, whilst the weaker one remains unmodified, thus occasioning the effects observed in quinicine and cinchonicine.

7. *Aricine* or *cinchovatine* ($C_{46}H_{26}N_2O_8$).—This base is less abundant than the two alkalies just described. It has been found in a white variety of cinchona bark, and has been but incompletely examined. Aricine crystallizes in white needles, which are fusible at 370°, but not volatile: it is soluble in ether; with nitric acid it strikes an intense and characteristic green colour.

(*b*) *Alkaloids contained in Opium.*

(1076) Opium, the inspissated milky juice of the *papaveraceæ*, is a very complicated substance, the composition of which varies greatly even when it is not adulterated, as it often is very largely. Genuine Smyrna opium is the best variety, since it contains the largest proportion of morphia. The following constituents, with the exception of opianine, have been ascertained to exist in most kinds of opium :—

	Meconic acid . . .	$3HO, C_{14}HO_{11}$	from 6 to 8 per cent.
Organic bases.	1. Morphia	$C_{34}H_{19}NO_6$	from 6 to 12 per cent.
	2. Codeia.	$C_{36}H_{21}NO_6$	less than 1 per cent.
	3. Thebaia	$C_{38}H_{21}NO_6$	Do.
	4. Papaverine	$C_{40}H_{21}NO_8$	Do.
	5. Opianine (normal narcotine?) . . .	$C_{42}H_{21}NO_{14}$?	(from Egyptian opium.)
	6. Narcotine (ethyl narcotine) . . .	$C_{46}H_{25}NO_{14}$	from 6 to 8 per cent.
	7. Narceia	$C_{46}H_{29}NO_{18}$	
	Meconine (opianyl) .	$C_{20}H_{10}O_8$	
	Resinous matter . .		
	Caoutchouc		4 or 5 per cent.
	Essential oil . . .		
	Mucilage or gum . .		

Many of the opium bases exhibit a very intimate relation to each other, although as yet the efforts of the chemist to transform them one into the other have been without success. Morphia, it will be observed, differs from codeia in containing one equivalent less of the compound (C_2H_2), although the two bases do not exhibit the close resemblance usually observed between the contiguous members of a homologous series. If the relation were one of ordinary homology, the action of iodide of methyl upon morphia should cause the production of codeia, just as dimethylia is produced from methylia by similar treatment; but instead of this the action of iodide of methyl upon morphia is attended with the formation of a new base of the ammonium class. Thebaia contains two equivalents more of carbon than codeia, and papaverine 2 equivalents more of carbonic oxide, 2 (CO) than thebaia, whilst opianine, if Gerhardt's interpretation of the results of Hinterberger be admitted, contains 2 equivalents of carbon and 6 of oxygen more than papaverine. The researches of Wertheim (*Journ. f. prakt. Chimie,* liii. 421), appear to have proved the existence of three homologous forms of narcotine in opium, and Gerhardt is disposed to view the opianine of Hinterberger (which is isomorphous with narcotine), as a fourth; these bases would then stand to each other in the following interesting relation:—

Opianine, or normal narcotine . . $C_{42}H_{20}(H)NO_{14} = C_{42}H_{21}NO_{14}$
Methyl-narcotine . . . . $C_{42}H_{20}(C_2H_3)NO_{14} = C_{44}H_{23}NO_{14}$
Ethyl-narcotine (ordinary narcotine) $C_{42}H_{20}(C_4H_5)NO_{14} = C_{46}H_{25}NO_{14}$
Trityl-narcotine . . . . $C_{42}H_{20}(C_6H_7)NO_{14} = C_{48}H_{27}NO_{14}$

thus constituting a true homologous series.

If opianine were distilled with hydrate of potash it probably would yield ammonia, whilst Wertheim has found the second of the foregoing compounds to furnish methylia, the third, ethylia, and the fourth, tritylia. Opianine has hitherto only been found in Egyptian opium, and has been but imperfectly examined.

The formula of narceia, as given by Anderson, differs from that of ordinary narcotine, in containing four equivalents more of water.

The opium alkalies, morphia, codeia, and papaverine, combine readily with iodine, and form crystallizable compounds containing three equivalents of iodine to one of the alkali. Codeia also unites with two equivalents of cyanogen, and forms a new and distinct base, *cyanocodeia.* True substitution compounds may also be obtained from codeia with the halogens, and with nitric acid, in which case one or more equivalents of hydrogen are displaced by a corresponding number of equivalents of chlorine, of bromine, or of peroxide of nitrogen.

(1077) *Isolation of the components of Opium.*—The separation of the opium bases from each other is a matter of considerable difficulty, and can only be performed satisfactorily when large masses of opium are acted upon. The following is an outline of the method to be adopted,—the morphia being first obtained by the process of Robertson and Gregory, and the mother liquors being afterwards treated for the other alkalies upon Anderson's plan (*Edinburgh Trans. Roy. Soc.* xx. 347, and xxi. 204):—

1. *Meconic Acid.*—An aqueous infusion of opium is prepared by mixing several pounds of the drug with three times its weight of water, straining the solution through linen, and treating the residue two or three times with fresh portions of water. An acid liquid is thus obtained, which is to be concentrated by evaporation,

and mixed with sufficient chalk to render it neutral; a solution of chloride of calcium containing a quantity of this salt equal to about one-twentieth of the weight of the opium employed, is then to be added. The precipitate which is thus occasioned consists of meconate of lime (1118), and must be separated by filtration.

2. *Narcotine.*—A large amount of narcotine remains in the portion of opium which is not soluble in water; it can be extracted by adding acetic acid to the mass, precipitating the filtered liquid by the addition of ammonia, and purifying the crude narcotine by digesting its solution in alcohol with animal charcoal, and recrystallizing.

3. *Morphia.*—The clear liquid filtered from the meconate of lime, is evaporated till it acquires the consistence of a thin syrup. On cooling, it becomes semisolid, from the formation of crystals of hydrochlorate of morphia; this salt may be purified by recrystallization, after the strongly coloured mother liquor has been separated from it by pressure.

4. *Codeia.*—On further concentrating the mother liquors from the hydrochlorate of morphia, a fresh crop of crystals is separated, which consists of a mixture of the hydrochlorates of morphia and codeia. If this be dissolved in hot water, and supersaturated with ammonia, the morphia is precipitated, while codeia remains in solution, mixed with muriate of ammonia. The hot aqueous solution is concentrated by evaporation, and on the addition of potash the codeia is separated, partly in the form of an oil which gradually becomes solid, and partly in crystals which are deposited as the liquid cools.

The black mother liquor from which the hydrochlorates of morphia and codeia have been separated, contains the whole of the remaining bases. It is to be diluted with water and filtered from flocculi of resinous matter which are thus got rid of, and ammonia is then to be added as long as a precipitate is occasioned. This precipitate (A) contains a large proportion of narcotine and of resin, with small quantities of thebaia and papaverine. The filtrate (B) contains narceine and meconine.

5. *Narceine.*—To the filtered liquid (B) a solution of acetate of lead is added, so long as it occasions a precipitate; a dirty brown colouring matter is thus thrown down, and is to be separated by filtration through a cloth; the excess of lead is removed by sulphuretted hydrogen, and the filtered liquid is concentrated by evaporation to a syrup, which on standing becomes filled with voluminous silky crystals of narceine; these may be purified by a second crystallization.

6. *Meconine.*—The mother liquor from the narceine is agitated with a fourth of its bulk of ether, and the ethereal solution is decanted; this process is repeated upon the aqueous portion, with fresh portions of ether, so long as the ether becomes coloured. The ethereal solutions are submitted to distillation, and, on the addition of water to the residue, a resinoid substance is separated, from which hydrochloric acid extracts a portion of papaverine. The undissolved portion, when crystallized from its solution in boiling water yields needles of meconine.

7. *Additional quantity of Narcotine.*—The precipitate (A) which was separated by ammonia from the mother liquors of the morphia and codeia, is at first granular, but if left in the press it soon concretes into a resinoid mass; in order to prevent this agglomeration, it must without delay be broken up and diffused through water, strained, again pressed, and the washings repeated until they run off nearly colourless. A portion of the precipitate is then boiled with rectified spirit, and the liquid filtered while hot; crystals of narcotine are deposited as it cools. The spirituous solution is then boiled with a fresh portion of the precipitate, and the same process is repeated until the whole of the precipitate has been so treated; the narcotine obtained in this manner can be added to that already procured from the undissolved mass (2).

8. *Thebaia.*—The spirituous mother liquor from which the narcotine has crystallized, now contains resinous matter, besides still retaining some narcotine, and all the papaverine and thebaia. The alcohol is distilled off, the bases are separated from the dark brown residue by means of acetic acid, and the solution thus obtained is decanted from the undissolved portion. On adding an excess of basic acetate of lead to the acetic solution, the whole of the papaverine, narcotine, and resin are precipitated. The excess of lead is next removed from the supernatant liquid, by the addition of sulphuric acid, and filtration; and, on then adding a slight excess of ammonia, impure thebaia is thrown down: it is purified by digestion with animal charcoal, and re-crystallization from alcohol.

9. *Papaverine.*—The greater part of the papaverine is contained in the precipitate which is separated from the acetic solution of thebaia by subacetate of lead. In order to isolate it, the precipitate is reduced to a fine powder, and boiled with alcohol. The alcohol is distilled off, and the dark brown residue is treated with dilute hydrochloric acid, and filtered from undissolved resin: the solution is then concentrated, and left to spontaneous evaporation;

crystals of hydrochlorate of papaverine are thus gradually formed, whilst the accompanying narcotine is retained in solution.

One of the greatest difficulties in the purification of the opium bases upon a small scale, arises from the presence of a peculiar resin in the drug; which, though not possessing the properties either of an acid or of a base, is readily soluble in dilute acids, and in solutions of potash, but sparingly so in ammonia. It is also soluble in alcohol, but insoluble in ether. It is fusible at a temperature considerably below that of boiling water. Aqueous solutions of opium contain it in considerable quantity, probably owing to the free acid which is present in the drug. On the addition of ammonia it is precipitated with the morphia and other bases; and, if the solution be heated, the resin fuses; thus occasioning the entire precipitate to agglomerate into a resinoid mass, which assumes the form of a brittle solid on cooling.

(1078) 1. Morphia ($C_{34}H_{19}NO_6$, 2 Aq).—This base occurs in combination with meconic, and, sometimes, with sulphuric acid. It appears to be the principal sedative constituent of opium, of which it constitutes from one-tenth to one-sixteenth by weight. In large doses it acts as a powerful narcotic poison.

Properties.—Morphia (so-called from Morpheus, in allusion to its narcotic properties) crystallizes generally in short, rectangular prisms, with two equivalents of water of crystallization. At a gentle heat the water is expelled, and the alkali melts into a resinoid substance, which solidifies into a radiated crystalline mass on cooling: by a higher heat it is decomposed. Morphia is soluble in about 1000 times its weight of cold, and in 400 of boiling water; the solution has a bitter taste, and changes the yellow colour of turmeric paper to brown. Boiling alcohol dissolves it abundantly, but it is insoluble in ether. Its alcoholic solution exerts a powerful rotation to the left upon a ray of polarized light. The fixed alkalies and alkaline earths, dissolve morphia without change, and deposit it in crystals as the solutions, by exposure to the atmosphere absorb carbonic acid. Ammonia dissolves it more sparingly. Concentrated nitric acid, when applied to a crystal, either of morphia, or of one of its salts, produces a lemon yellow or orange colour; and, ultimately, oxalic acid is formed. A mixture of nitric and sulphuric acid colours morphia green. When morphia is mixed with iodic, or with periodic acid, iodine is liberated, which may be recognised by its brown colour, and by the blue which it yields on the addition of a solution of starch. A neutral solution of perchloride of iron strikes with morphia a very characteristic blue colour, which is destroyed by an excess of acid. The salts of morphia give no precipitate with the gallates, but a copious curdy one with tannic acid and its salts. When morphia is heated to 400°, with hydrate of potash, an alkaline liquid distils over, containing ethylia. The salts of morphia crystallize readily; they are very soluble in water, and in alcohol, but are not soluble in ether. They have a bitter, disagreeable taste. If their solutions be mixed with tartaric acid, and supersaturated with bicarbonate of soda, no precipitate is formed.

Morphia appears to belong to the class of nitrile bases; since, when treated with iodide of ethyl, or with iodide of methyl, it yields salts of *ethylomorphium*, or of *methylomorphium*, corresponding to those of ammonium. Iodide of methylomorphium has the composition, $C_{34}H_{19}$ (C_2H_3) NO_6, I (How.)

Preparation.—Several methods are in use for extracting morphia from opium. On the large scale, Robertson's process, as modified by Gregory, and already described, is generally adopted. One of the simplest and best plans, if the operation be upon a small scale, is that proposed by Dr. Mohr; it is founded on the solubility of morphia in lime water, and the insolubility of the other bases in this liquid:—Each pound of opium is digested in 3 lb. of water, and boiled, and the liquid expressed from the undissolved portion, which is twice similarly treated; ¼ lb. of lime is boiled with 2 lb. of water, and the mixed opium infusions are added, in small quantities at a time, to the milk of lime, which is kept boiling; the liquid is filtered from the residue containing undissolved lime, and the other opium alkalies: this residue is twice boiled up with fresh water. The filtered liquids are mixed and evaporated down to two pints; again filtered; heated to boiling, and one ounce of powdered sal-ammoniac is added. By this means, the lime is neutralized, and the ammonia, as it is liberated, is volatilized at the high temperature employed: morphia is precipitated immediately, and increases in quantity as the liquid cools. The morphia thus obtained is of a deep brown colour. It is, therefore, re-dissolved in hydrochloric acid, again treated with milk of lime, and a second time precipitated by sal-ammoniac. The alkaloid, if the solution be dilute, is now deposited in beautiful crystals.

The *Hydrochlorate* $(C_{34}H_{19}NO_6, HCl, 6Aq)$ is the most important salt of morphia; it crystallizes in silky needles, and is readily soluble in water, especially if it contain a little free hydrochloric acid. It is also freely dissolved by alcohol. The *Acetate* was formerly a good deal used in medicine, but it has the disadvantage of being slightly deliquescent, and of losing acid when its aqueous solution is evaporated. The *Sulphate* ($C_{34}H_{19}NO_6$, HO, SO_3, 5Aq) crystallizes in tufts of colourless prisms. The *Citrate* is said to form the basis of the sedative medicine known under the name of the *Black drop*.

(1079) 2. Codeia ($C_{36}H_{21}NO_6$, 2Aq; Anderson).—Codeia (from κώδη, a poppy-head) appears, like morphia, to be one of the nitrile bases; since, when treated with iodide of ethyl, and then with oxide of silver, it yields a powerful alkaline base, of the ammonium class. It is contained in opium only in small proportion, for it does not amount to more than from one-fifteenth to one-thirtieth of the quantity of morphia. It has a powerful alkaline reaction, and is remarkable as being soluble in 80 parts of cold, and in 17 of boiling water: this solution throws down the oxides of lead, of copper, of iron, and of several other metals, from a solution of their salts. If codeia be boiled with less water than is necessary for its solution, it melts beneath the liquid to an oily-looking fluid. Codeia crystallizes from its aqueous solution in bold rhombic octohedra. If heated alone, its hydrated crystals lose 2 equivalents of water of crystallization, and undergo fusion at 300°. Both ether and alcohol dissolve codeia freely: the ethereal solution, by spontaneous evaporation, yields fine anhydrous prisms of the alkali. Its solutions exert left-handed rotation on a ray of polarized light. The caustic alkalies dissolve it but very sparingly: when distilled with potash, codeia yields ammonia, methylia, tritylia, and some other compounds still higher in this series of alcohol bases. The salts of codeia are practically unimportant: they have been carefully examined by Anderson, and they appear to have a powerful narcotic action when taken medicinally: they are not turned red by nitric acid, or blue by perchloride of iron, but are precipitated by infusion of galls. The hydrochlorate crystallizes with great facility.

3. *Thebaia*, or *Paramorphia* ($C_{38}H_{21}NO_6$).—This alkali crystallizes from its solution in alcohol or in ether, in square plates of silvery lustre, which have a styptic, acrid taste. It is poisonous when taken internally, and is said to produce tetanic symptoms, resembling those occasioned by strychnia. Thebaia is insoluble in alkaline liquids: it fuses at 257°: concentrated sulphuric acid colours it of a deep red: its salts do not crystallize readily.

4. *Papaverine* ($C_{40}H_{21}NO_8$) is distinguished from the other opium bases by giving with concentrated sulphuric acid a deep blue colour. It is sparingly soluble in cold alcohol, and is deposited from a hot alcoholic solution in small confused crystals.

It does not appear to exert any powerful effect upon the animal economy if taken internally.

(1080) 5. *Narcotine* ($C_{46}H_{25}NO_{14}$, 2Aq; Blyth; Wöhler).—The quantity of narcotine in opium varies from 6 to 8 per cent.: this body can hardly be said to possess alkaline properties. It is nearly insoluble in water, but is freely soluble in alcohol, and still more so in ether; its ethereal solution, by spontaneous evaporation, yields it crystallized in acicular groups, or in colourless, brilliant right rhombic prisms; these crystals are soluble in alcohol, and in the fatty and essential oils, but are insoluble in the caustic alkalies. Solutions of narcotine exert a powerful left-handed rotation upon polarized light: when the solution is acidulated, this rotatory power is reversed, and becomes right-handed. At 340° narcotine fuses, and loses water, and by a higher temperature it is decomposed. Acids dissolve it freely, but the solutions are decomposed by the addition of a large bulk of water: they are precipitated of a bright yellow on the addition of infusion of galls. A mixture of concentrated sulphuric and nitric acids produces a blood-red colour with narcotine and its compounds. Narcotine is less active as a poison than morphia; but, when administered to a dog in a dose of 23 grains, it speedily produced death. The salts of narcotine have a more bitter taste than those of morphia: the chloride and acetate crystallize with difficulty: most of its other salts form gummy compounds, which do not crystallize. The double salts with bichloride of platinum, and terchloride of gold, are, however, easily procured in crystalline scales. Allusion has already been made to Wertheim's discovery of three homologous forms of narcotine (1076). These different varieties of narcotine greatly resemble one another in character and properties, and are separated from each other with great difficulty. Narcotine is contained largely in the portion of opium which remains undissolved when treated with water. If this residue be digested with acetic acid, and the solution be supersaturated with ammonia, narcotine mixed with colouring matter is thrown down: it may afterwards be purified by solution in alcohol, and treatment with animal charcoal. If any of the acid solutions of narcotine be saturated with chloride of sodium, the liquid becomes turbid, and the narcotine is deposited in the course of a few days, in crystalline masses. This property has sometimes been taken advantage of, in the separation of narcotine from morphia.

Narcotine, under the oxidizing influence of bichloride of platinum or of peroxide of manganese, is decomposed, and gives rise to some very remarkable compounds (Wöhler; Blyth, *Liebig Annal.* L. 1 and 29; Anderson, *Trans. Roy. Soc. Ed.*, xx. 359). It appears to split up into a new base, termed *cotarnine*, and into opianyl, or into products which are the result of the decomposition of opianyl:—

$$\overbrace{C_{46}H_{25}NO_{14}}^{\text{Narcotine.}} + 2\,O = \overbrace{C_{26}H_{13}NO_6,\ 2\,Aq}^{\text{Cotarnine.}} + \overbrace{C_{20}H_{10}O_8}^{\text{Opianyl.}}.$$

If the oxidation be more energetic, the cotarnine is broken up into *apophyllic acid* (HO, $C_{16}H_9NO_8$), and ethylia; whilst the opianyl yields *opianic* and *hemipinic* acids:—

$$2\,(\overbrace{C_{20}H_{10}O_8}^{\text{Opianyl.}}) + 6\,O = \overbrace{HO,\ C_{20}H_9O_9}^{\text{Opianic Acid.}} + 2\,\overbrace{HO,\ C_{20}H_8O_{10}}^{\text{Hemipinic Acid.}}.$$

Cotarnine contains all the nitrogen of the narcotine. It forms fusible acicular crystals, which are sparingly dissolved by water, or by a solution of potash; but they are freely soluble in alcohol, ether, and solution of ammonia. Cotarnine is readily obtained by boiling a solution of narcotine in hydrochloric acid, with bichloride of platinum: the liquid becomes of a deep blood-red colour, and red crystals of the bichloride of platinum and hydrochlorate of cotarnine ($C_{26}H_{13}NO_6$, HCl + Pt Cl_2) are deposited: the base is easily procured by decomposing this salt with an alkali.

It will be unnecessary to enter into any minute description of the properties of the various products obtained by the oxidation of narcotine,* for they present but little intrinsic interest, although a knowledge of their composition, and of the mode of their formation, is essential towards the explanation of the rational composition of the group of alkaloids contained in opium. It would, for example, be interesting, to enquire whether the different varieties of narcotine yield a different alkali by oxidation: whether, in fact, as is probable, there are different varieties of cotarnine, into the composition of which methyl, ethyl, and trityl enter; and whether the colligate, opianyl, remains unchanged throughout the series.

6. *Opianyl*, or *Meconine* ($C_{20}H_{10}O_8$) may not only be formed by the oxidation of narcotine, but it exists in opium, in small quantity. This substance does not possess basic properties: it is freely soluble in boiling water, and crystallizes in white, inodorous, six-sided prisms, which are sparingly soluble in cold water, but are readily dissolved by alcohol, and ether. It fuses at 194° (230°, Anderson), and may be distilled without alteration. It is soluble in concentrated sulphuric acid, and the liquid becomes purple when gently

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* For details upon this subject, *vide* Anderson, Wöhler, and Blyth, *loc. cit.*

heated. Gerhardt considers this body as a *hydride of opianyl,* which stands in the same relation to opianic acid, that oil of bitter almonds does to benzoic acid (Gerhardt's opianyl* being $C_{20}H_9O_8$); thus :—

$$\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\H\end{matrix}\right\}}^{\text{Hydride of Benzoyl, or Oil of Bitter Almonds.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_{14}H_5O_2\\H\end{matrix}\right\}O_2}^{\text{Benzoic Acid.}} \ .$$

$$\overbrace{\left.\begin{matrix}C_{20}H_9O_8\\H\end{matrix}\right\}}^{\text{Hydride of Opianyl.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_{20}H_9O_8\\H\end{matrix}\right\}O_2}^{\text{Opianic Acid.}} \ .$$

Gerhardt's opianyl ($C_{20}H_9O_8$) also appears to enter into the formation of two remarkable compounds, derived from ammonia, which present the composition of amides. Anderson has termed them, respectively, *opiammon* and *teropiammon* : neither of them possesses basic characters.

$$\overbrace{C_{40}H_{19}NO_{16}}^{\text{Opiammon.}} = \left.\begin{matrix}C_{20}H_9O_8\\C_{20}H_9O_8\\H\end{matrix}\right\}N \quad ; \quad \begin{matrix}\text{obtained by evaporating}\\\text{a solution of opianate}\\\text{of ammonia.}\end{matrix}$$

$$\overbrace{C_{60}H_{29}NO_{26}}^{\text{Teropiammon.}} = \left.\begin{matrix}C_{20}H_9O_8\\C_{20}H_9O_8\\C_{20}H_9O_8\end{matrix}\right\}N,\ 2\,HO \ ; \quad \begin{matrix}\text{obtained by the action}\\\text{of dilute nitric acid}\\\text{upon narcotine.}\end{matrix}$$

In certain cases, when the oxidation of the narcotine was incomplete, a peculiar platinum salt was obtained by Blyth, which he believed to contain a base termed *narcogenine* ($C_{72}H_{38}N_2O_{20}$), but which he was unable to isolate; since immediately that it is liberated from its combinations, it breaks up into narcotine and cotarnine :—

$$\overbrace{C_{72}H_{38}N_2O_{20}}^{\text{Narcogenine.}} = \overbrace{C_{26}H_{13}NO_6}^{\text{Cotarnine.}} + \overbrace{C_{46}H_{25}NO_{14}}^{\text{Narcotine.}} \ .$$

(1081) 7. *Narceia,* or *Narceine.*—Two substances appear to have been described under this name; one of these, obtained by Pelletier, having the composition ($C_{32}H_{19}NO_{10}$); the other examined by Anderson, being ($C_{46}H_{29}NO_{18}$). The latter is a feeble base, which is soluble in boiling water, and crystallizes from a hot solution as it cools, in delicate silky needles, which are soluble in alcohol, but insoluble in ether: at 197° it fuses, and, at a somewhat higher temperature it becomes decomposed. It combines with the dilute acids, forming crystallizable salts. Concentrated sulphuric acid dissolves narceine with an intense red colour, which, when gently heated, passes into green. Iodine colours the base of a deep blue, which disappears on the addition of an alkali.

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* This practice of employing terms already appropriated to previously known substances, to indicate other compounds, is greatly to be deprecated.

(c) *Alkali obtained from the Pepper tribe.*

(1082) *Piperine* ($C_{68}H_{38}N_2O_{12}$?).—This is a substance possessed of feeble basic properties. It is found in the common white and black pepper, and in long pepper. White pepper easily yields it when treated with alcohol, which extracts a resinous matter with the piperine, from which the latter may be freed by digestion in a solution of potash : the piperine which remains undissolved is recrystallized from alcohol, and furnishes colourless prisms, which are fusible at 212°. Piperine is nearly insoluble in cold water; it has an acrid taste, resembling that of pepper : the hydrochlorate is its most stable salt. Concentrated sulphuric acid dissolves piperine, with a red colour; but the base is precipitated unchanged, on dilution with water. Nitric acid acts powerfully on piperine, developing an odour of bitter almonds, whilst a brown resin rises to the surface. On evaporating the solution to dryness, a brown residue is left, which, when treated with potash yields a magnificent blood-red liquid; and, on distilling this mixture it furnishes *piperidine*, which is a powerfully alkaline base. The same base is also obtained when piperine is distilled with three times its weight of hydrate of potash, at a temperature not exceeding 320°. The piperidine ($C_{10}H_{11}N$), being volatile, passes over, and a yellow, resinoid azotized acid remains in combination with the potash.

Piperidine ($C_{10}H_{11}N = C_{10}H_{10}, H, N$) *Sp. gr. of vapour* 2·982. —This is a remarkable oily base, with a pungent odour, recalling both that of ammonia, and that of pepper: it boils at about 223°. It resembles ammonia in alkaline power, and precipitates many metallic oxides from their salts. It combines with the acids, neutralizing them, and forming well crystallized salts: with cyanic acid it forms a compound urea, *piperyl-urea*; and, if heated with cyanic ether, piperidine forms a compound termed *ethyl-piperyl-urea*.

Urea	H_4N_2,C_2O_2
Piperyl-urea	$H_2(C_{10}H_{10})\ N_2,C_2O_2$
Ethyl-piperyl-urea	$H,\ C_4H_5\ (C_{10}H_{10})\ N_2,C_2O_2$

One of the equivalents of hydrogen in piperidine may be displaced by ethyl or by methyl, on treating the base with iodide of ethyl or of methyl; and ethyl-piperidine, by treatment with an additional quantity of the hydriodic ether, yields the iodide of an ethyl base corresponding to tetrethylium.

Capsicine is the name given to an alkaloid obtained from the Cayenne pepper. It has a burning taste; and as usually prepared, it presents a resinous appearance; but, when quite pure, it may be crystallized. It forms crystallizable salts with acetic, nitric, and sulphuric acids.

(*d*) *Alkaloids from the Strychnos tribe.*

(1083) The fruit and bark of the *Strychnos nux vomica*, and other parts of several plants of this tribe, particularly the seeds of the *strychnos ignatii*, contain two alkalies closely related to each other: both of them act as powerful poisons on the living frame, and speedily occasion death, amid violent tetanic convulsions: these bases are *strychnia* and *brucia*. They contain 2 equivalents of nitrogen in each equivalent of base. In the *nux vomica* they occur in combination with lactic acid, and a peculiar vegetable acid. In order to extract them from this fruit, the following method may be adopted:—The rasped seeds are boiled with 4 times their weight of alcohol, acidulated with 1 per cent. of sulphuric acid. The alcoholic liquid is neutralized with lime in slight excess: the acid and colouring matters are thus precipitated, whilst the bases remain in solution; the alcohol is distilled off, and the residue treated with acidulated water, from which, on the addition of ammonia, the strychnia and brucia are precipitated. The two alkalies are separated by converting them into nitrates, and crystallizing; the nitrate of strychnia, being the least soluble of the two, is first deposited. Both strychnia and brucia exert a left-handed rotatory effect upon a ray of polarized light; but the rotatory power of strychnia is twice as great as that of brucia.

(1084) STRYCHNIA ($C_{42}H_{22}N_2O_4$) is contained in the St. Ignatius' bean, to the extent of nearly 1½ per cent.; and it is one of the active constituents of the upas poison. Strychnia is one of the most powerful of the vegetable bases; it precipitates many metallic oxides from their salts, either completely or partially: in the latter case, it forms double salts,—such as the double sulphate of strychnia and copper, which crystallizes in long green needles. Strychnia crystallizes from dilute alcohol, in white anhydrous octohedra, or in square prisms, which do not fuse on the application of heat. It is insoluble in absolute alcohol, ether, and the caustic alkalies; but it is soluble in the essential oils, and in chloroform. Cold water does not dissolve more of it than $\frac{1}{7000}$th of its weight; but this solution, even when diluted with 100 parts of water, still possesses a distinctly bitter taste. If distilled with hydrate of potash, strychnia, like cinchonia and quinia, yields the oily base quinoline. A portion of the hydrogen in strychnia may be displaced by chlorine or by bromine, and the body thus obtained still retains basic properties. Strychnia, when triturated with iodine, forms a peculiar crystalline compound, which is soluble in alcohol, and yields orange-coloured scales $2\,(C_{42}H_{22}N_2O_4)\,I_3$, from which the acids separate strychnia, unaltered. This compound is analogous to those which iodine yields with the opium bases (1076). Strychnia, when pure, is turned yellow by concentrated nitric acid, and yields a nitrate of a new substitution base, nitrostrychnia. If brucia be present with the strychnia, as is usual in most commercial specimens, the colour produced by nitric acid is deep orange, or red. With iodide of ethyl, strychnia yields the iodide of *ethylostrychnium* ($C_{42}H_{22}, C_4H_5, N_2O_4\ I$), from which oxide of silver separates a hydrated oxide of an ammonium base ($C_{42}H_{22}, C_4H_5, N_2O_5, HO$), which is crystallizable: strychnia is therefore a nitrile base.

Salts of strychnia.—Sulphuric acid forms a neutral and an acid salt with strychnia; the crystals of the neutral sulphate ($C_{42}H_{22}N_2O_4$, HO, SO_3, 7 Aq) are square prisms. Solutions of the salts of strychnia yield a precipitate with infusion of galls. If a slight excess of tartaric acid be added to the solution of a salt of strychnia, and then one of bicarbonate of soda or potash, the strychnia is gradually deposited in crystals. A solution which does not contain less than $\frac{1}{375}$th its weight of the base gives on the addition of a strong solution of sulphocyanide of potassium, tufts of crystals, after the lapse of a few minutes. A minute quantity of strychnia with concentrated sulphuric acid, and a fragment of peroxide of lead, or what is still better, of bichromate of potash, gives a beautiful violet tint, which gradually fades into a pale rose colour; other oxidising agents produce a similar effect. With solution of perchloride of gold, salts of strychnia give a bright blue colour. The presence of strychnia may be detected in very minute quantities of complicated organic liquids, by rendering them alkaline with potash, and agitating thoroughly with a few drachms of chloroform; the chloroform dissolves the strychnia, and leaves it in the solid form on evaporation; from this residue it may be extracted by dilute hydrochloric acid; and it may afterwards be submitted to the usual tests.

(1085) *Brucia* ($C_{46}H_{26}N_2O_8$, 8 Aq; Regnault) is more soluble in water, and in strong alcohol, than strychnia. This alkali is contained in *nux vomica* in larger quantity than strychnia. It may also be readily obtained from the false angustura bark, which does not appear to contain any strychnia, but furnishes brucia more abundantly than the beans of the *nux vomica*. Brucia crystallizes in colourless, transparent, oblique, rhombic prisms, which are insoluble in ether. Brucia melts readily on the application of heat, and loses its water of crystallization. It is less active as a poison than strychnia. Its salts have a bitter taste, and may be distinguished from those of strychnia, after they have been mixed with tartaric acid, by not yielding any precipitate on the addition of bicarbonate of soda. This base is further distinguished from strychnia by the bright scarlet colour gradually passing into yellow, which brucia or any of its salts gives with nitric acid; if a little protochloride of tin be added, a beautiful violet colour is produced.

The action of nitric acid upon brucia is attended with the production of definite results, from which it appears probable that methyl enters into the composition of this base. When the concentrated acid is poured upon brucia, the mixture assumes a deep red colour, becomes hot, and emits a colourless gas, which has the peculiar smell of apples, and a portion of which is soluble in water and in alcohol. This gas consists of a mixture of nitrite of methyl with binoxide of nitrogen and carbonic acid, the carbonic acid being the secondary result of the decomposition of oxalic acid, which is found in the liquid, accompanied by a new substance termed *cacotheline;* this body is a nitro-substitution compound, of feeble basic properties. Strecker represents the action of nitric acid upon brucia by the following equation:—

$$\overbrace{C_{46}H_{26}N_2O_8}^{\text{Brucia.}}+\overbrace{5(HO,NO_5)}^{\text{Nitric Acid.}}=\overbrace{C_2H_3O,NO_3}^{\text{Nitrite of Methyl.}}+\overbrace{2HO,C_4O_6}^{\text{Oxalic Acid.}}+\overbrace{C_{40}H_{22}(NO_4)_2N_2O_{10}}^{\text{Cacotheline.}}$$
$$+\ 2NO_2\ +\ 4HO.$$

A further proof of the presence of methyl in brucia is found in the fact, that when this base is distilled with dilute sulphuric acid and peroxide of manganese, or with chromate of potash and sulphuric acid, formic and carbonic acids are produced, and an inflammable liquid passes over, burning with a blue flame, and presenting the properties of wood spirit.

Igasurine.—This name has been given to a third alkali, recently discovered in *nux vomica.* It is more soluble in water than either strychnia or brucia. The *woorara* poison of South America appears to be obtained from a plant of the strychnos tribe; it acts as a fatal poison if introduced into the blood by a wound, but it may be swallowed with impunity.

(*e*) *Other less known Bases.*

(1086) The bulbs of the *colchicum autumnale,* and the roots and seeds of different species of *veratrum* contain several alkaloids, the most important of which, *veratria*, has been employed medicinally. Veratria ($C_{64}H_{52}N_2O_6$; Merck) occurs principally in combination with gallic acid; it is an extremely acrid and violent poison, producing dangerous fits of sneezing if it come in contact, even in minute quantity, with the mucous membrane of the nose. It acts as a valuable sedative in some cases of neuralgia if applied in the form of ointment to the surface of the body. Veratria is almost insoluble in water and in alkaline solutions; alcohol dissolves it freely, and deposits it by spontaneous evaporation in long delicate needles. Ether dissolves it with difficulty; fuming sulphuric acid colours it yellow, then blood-red, and lastly, violet. Nitric acid strikes with it a red which after a time becomes yellow. Three other poisonous bases, *sabadillia, colchicia,* and *jervia,* are found, along with veratria, in the *veratrum album,* or white hellebore. Jervia ($C_{60}H_{45}N_2O_5$, 4 aq) is white, crystalline, and fusible.

Aconitina is another intensely poisonous alkaloid, which is employed medicinally, but the composition of which is uncertain; it is obtained from various species of monkshood or aconite. It crystallizes with difficulty, and is more soluble in water than most of these bases; it is dissolved easily by alcohol and ether. These solutions have a powerfully alkaline reaction; and the base forms perfectly neutral salts, which when moistened with concentrated sulphuric acid acquire a colour which at first is yellowish, and then becomes of a dirty violet red.

Many of the *solanaceæ* and *umbelliferæ* contain alkaloids. The henbane (*hyoscyamus niger*) and both the common and the deadly nightshade (*solanum dulcamara*, and *atropa belladonna*) owe their poisonous qualities to compounds of this kind.

Atropia ($C_{34}H_{23}NO_6$; Planta) crystallizes in colourless silky needles, which are freely soluble in alcohol and in chloroform, but less so in ether. The crystals fuse at 194°, and undergo sublimation and partial decomposition at 284°. Solutions of atropia are speedily altered by evaporation when exposed to the atmosphere. Atropia is present in all parts of the belladonna, but is commonly extracted from the root. It appears to be identical with *daturia*, the active principle contained in the seeds of the *datura stramonium*. The salts of atropia are bitter, acrid, and highly poisonous, producing a remarkable dilatation of the pupil of the eye.

In addition to these bases two others may be mentioned, viz., *harmaline* and *harmine*, which are found probably combined with phosphoric acid, in the seeds of the *peganum harmala*, a plant extensively grown in Southern Russia. It is used in dyeing silk, to which it imparts various shades of pink, rose, or red. *Harmaline* ($C_{26}H_{14}N_2O_2$) when pure crystallizes in colourless prisms, but they generally retain a brownish yellow tint, and tinge the saliva yellow. It has a bitter, astringent, acrid taste; it is freely soluble in alcohol, but sparingly so in water and in ether. It is fusible and volatile; with acids it forms yellow, very soluble, crystallizable salts. Oxidizing agents transform it into a red colouring matter which combines with acids, forming salts which constitute the basis of the *harmala red* of commerce. Harmaline contains two equivalents more of hydrogen than *harmine* ($C_{26}H_{12}N_2O_2$), into which it may be converted by oxidation: harmine crystallizes in long delicate prisms; it forms colourless salts, which are quite neutral.

Emetia, the active principle of ipecacuanha, also possesses the properties of a feeble base: it is nearly insoluble in water and in ether, but is readily soluble in alcohol and in dilute acids; chloroform also dissolves it with facility. It is a powerful poison, and acts as a violent emetic in doses of the one-sixteenth of a grain or less. It fuses readily, and is accompanied in the ipecacuanha root by a large proportion of oily matter, which emits a feeble odour of tobacco when heated. The base is easily obtained by treating the alcoholic extract of the root with dilute sulphuric acid, filtering from the oily matter, and after slightly supersaturating the solution with ammonia, agitating the turbid liquid with chloroform. On evaporating the chloroform, the emetia is left as a yellowish resinous-looking mass. It may be purified by conversion into a salt, and digesting its solution with a small quantity of animal charcoal; on adding an alkali to the filtered liquid the emetia is precipitated. The salts of emetia do not readily crystallize.

(*f*) *Alkaloid of Coffee and Tea.*

(1087) CAFFEINE or THEINE ($C_{16}H_{10}N_4O_4$, 2 aq).—This substance occurs in tea, in coffee, and in *maté,* a shrub used by the natives of Paraguay and a large number of the inhabitants of South America, for making an infusion which they substitute for tea. It is also contained to the extent of 5 per cent. (Stenhouse) in *guarana,* an astringent species of chocolate prepared from the fruit of the *paullinia sorbilis.* Tea appears to contain from 2 to 4 per cent. of caffeine (Péligot), but the quantity of it in coffee, according to Stenhouse, seldom exceeds 1 per cent.

Caffeine is easily obtained from tea by making a strong infuby two equivalents of methyl, and cholestrophan bears a similar relation to parabanic acid:—

Alloxantin	$C_8H_5N_2O_{10} = C_8H_3N_2O_8, 2HO$
Amalic acid (dimethyl-alloxantin)	$C_8H(C_2H_3)_2N_2O_8$
Parabanic acid	$2\,HO, C_6N_2O_4 = C_6H_2N_2O_6$
Cholestrophan (dimethylo-parabanic acid)	$C_6(C_2H_3)_2N_2O_6$

Amalic acid also possesses the property, like alloxantin, of staining the fingers pink; and if exposed to the vapour of ammonia, it produces a compound homologous with murexid, which like the latter compound, is distinguished by its magnificent purple colour:—

Murexid	$C_{24}H_{12}N_{10}O_{16}$
Caffeo-murexid	$C_{36}H_{24}N_{10}O_{16}$

In the latter case the difference between the two compounds is 3 (C_4H_4), because murexid is the result of a reaction of ammonia upon three equivalents of alloxantin, and caffeo-murexid in like manner is derived from three equivalents of amalic acid.

(1088) *Chemical and dietetic characters of Coffee and Tea.*—Caffeine is a compound which presents a high degree of interest both from the metamorphoses of which it is susceptible, and from the circumstance that it forms an ingredient in three substances, namely, tea, coffee, and a third substance of less importance, *maté* (or Paraguay tea, obtained from the *Ilex Paraguayensis*), one or other of which constitutes a portion of the daily diet of three-fourths of the human race. The circumstance that these different shrubs should have been selected by different nations, for the purpose of yielding a beverage, when infused with boiling water, shows that the ingredient which they furnish is one which is adapted in a special manner to some craving of the human frame. Although these bodies differ so widely in flavour, they all contain the same azotised principle, the physiological effects of which have not been submitted to the detailed examination which they well deserve. The best series of experiments upon this point are due to Julius Lehmann, who watched for some weeks the effects of roasted coffee, as well as of its essential oil, and of caffeine, upon two individuals in good health (Liebig's *Annal.* lxxxvii. 205). The use of coffee as an article of diet appears to exercise an important influence in retarding the waste of the tissues of the body; since it was found that during its use, the proportion of phosphoric acid and of urea excreted by the kidneys, was much smaller than when the coffee was omitted, the diet being in all other respects the same in both cases. Thus, it was found that when an infusion of three-quarters of an ounce of roasted coffee berries was taken daily for a fortnight, the average proportion of urea and of phosphoric acid which passed off by the kidneys in 24 hours, was less by one-third than it was during a similar period in which the coffee was omitted. The empyreumatic oil of the coffee was found to exert a stimulating effect upon the nervous system. When too large a quantity of this essential oil was taken it produced loss of sleep, nervous excitement, and symptoms of congestion of the brain. In smaller quantities it produced a gentle perspiration, removed the sensation of hunger, and acted upon the bowels as a laxative. It likewise reduced the amount of urea and of phosphoric acid in the urine. It was also concluded from the production of similar alterations in the quality of the urine, when a solution of pure caffeine was substituted for the ordinary infusion of coffee, that caffeine likewise exerted a power of retarding the disintegration of the constituents of the animal frame.

Tea, coffee, and the Paraguay tea-plant, in the form in which they are used dietetically, all contain the following principles:— 1. Caffeine. 2. One of the forms of tannic acid. 3. An aromatic essential oil, which is different in each plant, and is the main cause of their different and peculiar flavours.

Constituents of Coffee.—When the coffee berry is first gathered and dried in the air, it has but little fragrance, and only a slightly bitter and astringent taste. The raw coffee berry is hard and horny; it swells up with difficulty even when heated with boiling water; it contains in its green state about the same quantity of soluble matter as after it has been roasted; but the amount varies greatly in different specimens.

Coffee swells considerably during roasting, the increase in volume amounting to one-third or even to one-half of its original bulk; at the same time it loses in weight to an extent varying from 15 to 25 per cent. upon the weight of the berries before roasting; the amount of this loss depending upon the extent to which the roasting is carried. The roasting should be stopped as soon as the berry has become friable. The agreeable bitter aromatic taste of coffee is developed during this operation. It is worthy of remark that inferior coffee becomes improved in quality by keeping, and if roasted after it has been kept for some years, it yields an infusion of a finer flavour than if roasted immediately after it had been gathered. Both the essential oil and the bitter flavour are developed from one of the soluble constituents of the berry, since the aqueous extract of the raw berry when roasted acquires the full odour and taste of coffee. The proportion of this aromatic oil in roasted coffee is very minute; not exceeding, according to Payen, one five-thousandth of the weight of the coffee. Coffee also contains a considerable quantity of fixed oil. The astringent acid, *caffeic acid,* as it has been termed, constitutes about 5 per cent. of the dry berry: it does not blacken the solution of protosulphate of iron, but turns it green, and it does not precipitate solutions of gelatin; it is dissolved by strong sulphuric acid and produces a red liquid. When exposed to the air in contact with alkalies, caffeic acid absorbs oxygen and forms a yellow insoluble resin. A peculiar reaction occurs with caffeic acid when its solution is heated with four times its weight of black oxide of manganese, and one part of oil of vitriol diluted with an equal bulk of water. Yellow crystals of kinone (1127) are deposited upon the neck and sides of the retort, and the acid liquid which distils over is saturated with kinone, and contains formic acid. (See a Report on the adulterations of coffee by Graham, Stenhouse, and Campbell; *Q. J. Chem. Soc.* ix. 52.) The acid of Paraguay tea, and that of the leaves of the holly tribe, also furnish kinone by similar treatment. The following is the average composition of the coffee berry, according to Payen:—

Ligneous tissue	34·0
Hygroscopic water	12·0
Fixed fatty matters	10 to 13·0
Gum, sugar, and a vegetable acid	15·5
Azotised matter, analogous to legumin	13·0
Free caffeine	0·8
Compound of caffeine with potash and chlorogenic (caffeic) acid[*]	3·5 to 5·0
Aromatic essential oil	0·002
Solid fatty essence	0·001
Saline matters	6·697

The saline matters contained in coffee contain more than half their weight of potash (51·5 to 55·8 per cent.) chiefly in the form of carbonate and phosphate; they are almost entirely free from silica. The sugar in raw coffee is in the form of cane sugar (Graham, Stenhouse, and Campbell), and its quantity varies from 6·2 to 7·7 per cent. The process of roasting not only expels the greater part of the hygroscopic moisture, but it considerably modifies the properties of the caffeic acid, and converts nearly the whole of the sugar into caramel. The solid portion left after infusing the ground berry in water contains a large amount of nutritious substance, in the form of an azotised principle resembling casein or legumin. This may account for the practice among the Arabs and other oriental nations, of swallowing the undissolved portions of the grain with the decoction: in the countries of Central Asia the use of animal food is rare, and hence the inhabitants have been led to vary the mode of preparing their coffee in such a manner as to enable them to use the substance in some measure as a substitute for the nitrogenous constituents supplied by a flesh diet.

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[*] Containing 39 per cent. of caffeine; 3·5 parts, therefore, indicate 1·01 of caffeine. This salt has not been found by other chemists.

The dried leaves of the coffee plant also contain as much as 1½ per cent. of caffeine (Stenhouse), as well as an astringent vegetable acid, and a large proportion (13 per cent.) of an azotised principle allied to gluten. The dried coffee leaf has an agreeable aroma; it is used largely in the form of infusion by the natives of Sumatra, who prefer it as a beverage, to that prepared from the coffee berry.

Constituents of the Tea-plant.—The dried leaves of the *Thea Sinensis*, which constitutes our ordinary "tea," contain about 45 per cent. of soluble matter; but, according to Péligot, tea does not usually give up more than about one-third of its weight of soluble matter to boiling water. The most important constituents of the leaf, in the form in which it is consumed in Europe, are:—1. *The essential oil*, to which it owes its peculiar aroma, and the proportion of which, according to Mulder, is about 0·79 in green, and 0·60 per cent. in black tea. This oil exerts a most powerfully stimulating and intoxicating effect. In China, tea is seldom used till it is a year old, on account of the well-known intoxicating effects of new tea, due probably to the larger proportion of essential oil contained in the freshly dried leaf. 2. *Caffeine*, or theine, the quantity of which varies considerably in different varieties of tea; different kinds of green tea furnished to Péligot, amounts ranging from 2·2 to 4·1 per cent. 3. A ***nitrogenised compound*** analogous to casein, amounting to 14 or 15 per cent. of the weight of the leaf. Almost the whole of this material is thrown away in the spent leaves, which when dry, contain not less than 28 per cent. of their weight of this substance.* 4. *The astringent principle*, which is a modification of tannin; it occasions a precipitate in solutions of gelatin, and produces a black with protosulphate of iron: it constitutes from 13 to 18 per cent. of the dried leaf. The ash of tea varies from 5·3 to 5·6 per cent. of the dried leaf; a portion of this ash is probably due to the colouring matter which the Chinese are in the habit of adding to their green teas, for the foreign market; this colouring matter is in some cases indigo, in others a mixture of Prussian blue and pipe clay.

It appears from the observations of Mr. Fortune, that either green or black tea can be obtained at pleasure from the same plant. *Green tea* is prepared from the young leaves, which, within an hour or two after they have been gathered, are roasted in pans over a brisk wood fire. After four or five minutes' roasting the leaves become flaccid, and are rolled by the hands upon a wooden table; after which they are again thrown into the drying pans, where they are kept in rapid motion, and in about an hour, or an hour and a half, are completely dried.

Black tea is allowed to lie in heaps for ten or twelve hours after the leaves have been gathered; they are then tossed about for some time till they become flaccid. At this stage they begin to emit a fragrant smell; they are next rolled in balls, with the hand, upon a wooden table, and a large quantity of liquid is expressed from them, after which they are shaken out, roasted for a few minutes, again rolled; and, whilst still flaccid, are exposed to the air for some hours upon shallow bamboo trays: this alternate heating and rolling is repeated three or four times; and, finally, the leaves are slowly dried over charcoal fires. A species of fermentation appears to occur during the drying of the leaf, in consequence of which a development of essential oil takes place, by which the agreeable aroma is occasioned: this aroma is wanting in the fresh leaf. The change of the leaf from green to black, is mainly due to chemical alterations produced by the oxygen of the air upon the constituents of the leaf, and especially upon the astringent principle; this change being prevented in green tea by the rapid process of drying to which it is subjected.

(1089) *Theobromine* ($C_{14}H_8N_4O_4$).—This body is present in chocolate; it is homologous with caffeine, but it contains (C_2H_2) less than this substance. It is extracted from the cacao nut (*Theobroma Cacao*) by a process similar to that employed in obtaining caffeine. Theobromine is but sparingly soluble in boiling water, and still less so in alcohol and in ether: it has a slightly bitter taste. At a high temperature it may be sublimed, a part of it undergoing decomposition during the process. It resembles caffeine in its power of forming crystallizable salts with some of the acids; but these compounds are decomposed by water, and its basic powers are very feeble.

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* The Mongol Tartars economise a large portion of this nutritive matter by boiling the powdered tea with the alkaline water of their steppes, to which a quantity of salt is added; by this means a notable quantity of the gluten is dissolved or suspended in the liquid, which they commonly eat thickened with butter, milk, and baked flour (Lehmann).

The cacao nut is remarkable for the large proportion of fatty matter which it furnishes. This fat is not liable to become rancid, a circumstance which adds greatly to the value of the nut as an article of food. The nut, when deprived of its husk, is said to contain nearly 56 per cent. of this fat, 17 per cent. of a substance resembling gluten, and 22 of starch, gum, sugar, and ligneous tissue. The aromatic flavour of cocoa is due to the roasting to which the nut is subjected, previous to grinding it. If the roasted nut be simply crushed after it has been freed from its husk, it forms the *cocoa nibs* of the grocer. *Chocolate* is prepared by grinding the roasted nut into a paste between hot rollers, and mixing it with sugar, vanilla, cinnamon and other spices.

The number of well-defined bases of animal origin is but small, and as they are generally produced by the decomposition of azotised compounds not as yet described, it will be more convenient to defer their consideration till a later period.

CHAPTER V.

ON THE ORGANIC ACIDS.

§ 1. *General remarks on the Organic Acids, Oxychlorides, Anhydrides, and Ketones.*

(1090) THE ORGANIC ACIDS constitute an extremely numerous and important class of compounds; but many of them are so intimately related to a large number of other well-defined natural groups, that it would be far from advantageous to detach each acid from the group to which it properly belongs, for the sake of describing it with other bodies to which, often, it may bear little resemblance save in the circumstance that, like them, it possesses the power of forming salts with bases. Accordingly, several of these bodies have already been described in the previous sections, where they seemed to be naturally connected with the compounds under examination; and, although it will be convenient to associate together certain of the acids in the present chapter, the consideration of others will be postponed until the substances to which they are most nearly allied pass under review.

At present no organic alkali is known, into the composition of which nitrogen does not enter; so that if it be ascertained that nitrogen is absent from any particular compound, it may at once be concluded that the body in question cannot belong to the class of organic bases; but there is no elementary substance with the presence of which the acid character can be thus specifically connected: and no general law of composition has hitherto been arrived at, by which it is rendered possible from a knowledge of the empirical formula of a substance, to predict that it will possess the properties of an acid.

(1091) *Monobasic and Polybasic Acids.*—The organic acids may be subdivided into *monobasic* and *polybasic* (1102); the important group derived from the alcohols by oxidation, furnishing a good illustration of the monobasic acids; whilst some of the more important and widely diffused vegetable acids, such as the citric, the tartaric, and the malic, afford examples of the polybasic class.

A. *Monobasic Acids.*—Most of the monobasic acids are compounds which, in their condition of *normal acids,* or *normal hydrates,** that is to say in their form of monohydrates, are bodies which contain either four or six equivalents of oxygen; and they fall under some of the following general formulæ; in which, for the sake of simplicity, the basic water is incorporated with the other constituents of the acid; *n* is in all cases an even number.

	a.		*b.*
1.	$C_nH_n\ O_4$	1.	$C_nH_n\ O_6$
2.	$C_nH_{n-2}O_4$	2.	$C_nH_{n-2}O_6$
3.	$C_nH_{n-4}O_4$	3.	$C_nH_{n-4}O_6$
4.	$C_nH_{n-6}O_4$	4.	$C_nH_{n-6}O_6$
5.	$C_nH_{n-8}O_4$	5.	$C_nH_{n-8}O_6$
6.	$C_nH_{n-10}O_4$	6.	$C_nH_{n-10}O_6$

1. *Normal acids which contain four equivalents of oxygen.*—These are of much more frequent occurrence than any other form of acids; and of these, the class which is indicated by the for-

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* Normal acetic acid, for instance, is $HO, C_4H_3O_3$, or $C_4H_4O_4$

mula *a.* 1, ($C_nH_nO_4$) is the most numerous. The volatile fatty acids mentioned at page 31, belong to this series.

There are also several well-known acids which have the composition of the formula, *a.* 2, ($C_nH_{n-2}O_4$), viz. :—

Acrylic Acid	$C_6H_4O_4$	Physetoleic	$C_{32}H_{30}O_4$
Angelic	$C_{10}H_8O_4$	Oleic and Elaidic	$C_{36}H_{34}O_4$
Campholic	$C_{20}H_{18}O_4$	Doeglic	$C_{38}H_{36}O_4$
Moringic	$C_{30}H_{28}O_4$	Erucic	$C_{44}H_{42}O_4$

Many of these acids exhibit that close resemblance to each other in properties, which is always observed in bodies belonging to the same homologous series.

No acids corresponding to the formula *a.* 3, ($C_nH_{n-4}O_4$) have as yet been discovered; and only one, the oxyphenic ($C_{12}H_6O_4$), which belongs to the group *a.* 4, ($C_nH_{n-6}O_4$); but the group *a.* 5, ($C_nH_{n-8}O_4$) contains several interesting acids, the last three being homologous compounds: these acids are sometimes spoken of as the *aromatic acids.* They are the following :—

Salicylous acid	$C_{14}H_6O_4$	Toluic acid	$C_{16}H_8O_4$
Benzoic acid	$C_{14}H_6O_4$	Cuminic acid	$C_{20}H_{12}O_4$.

The group *a.* 6, ($C_nH_{n-10}O_4$) contains

Cinnamic acid	$C_{18}H_8O_4$	Pinic acid	$C_{40}H_{30}O_4$?

2. *Normal acids which contain 6 equivalents of oxygen.*—These are comparatively few in number. None are yet known of the formula *b.* 1, ($C_nH_nO_6$). To the formula *b.* 2, ($C_nH_{n-2}O_6$) ricinolic acid ($C_{36}H_{34}O_6$) may be referred.

The only compound of the formula *b.* 3, ($C_nH_{n-4}O_6$) is

Guaiacic Acid . . . . $C_{12}H_8O_6$.

To the class *b.* 4, ($C_nH_{n-6}O_6$) belong the isomeric compounds

Pyromucic acid	$C_{10}H_4O_6$.
Pyromeconic acid	

The group *b.* 5, (C_nH_{n-8}, O_6) is more numerous, and the last two acids are closely related to each other:

Ampelic acid	$C_{14}H_6O_6$	Anisic acid	$C_{16}H_8O_6$.
Salicylic acid	$C_{14}H_6O_6$		

The series *b.* 6, ($C_nH_{n-10}O_6$) is at present represented by a single acid, viz.—

Coumaric acid . . . . $C_{18}H_8O_6$;

but both this and the preceding group are intimately connected with the acids of the formula *a.* 5, and *a.* 6, from which the acids of the corresponding group in the column *b* (p. 299), with 6 equivalents of oxygen, would be formed by a simple act of oxidation.

3. *Acids not belonging to any of the foregoing groups.*—The various acids formed by substitution from others of known composition, such for example as

Nitranisic acid	$C_{16}H_7,NO_4,O_6$
Trichloracetic acid	$C_4HCl_3O_4$
Bromo-salicylic acid . . .	$C_{14}H_5BrO_6$

may be fairly considered as belonging to one of the groups just indicated; but a considerable number of monobasic acids exist, such as carbolic or phenic ($C_{12}H_6O_2$) and amygdalic ($C_{40}H_{27}O_{25}$) acids, which are not included in any of the foregoing groups.

The numerous acids obtained from the bile, and the acids connected with the colouring matters of the lichens are also not mentioned in these groups; neither are the various acids which contain nitrogen; such, for example, as

Amalic acid .	$C_{12}H_7N_2O_8$	Aspartic acid	$C_8H_7NO_8$
Isatic acid .	$C_{16}H_7NO_6$	Carbazotic acid	$C_{12}H_3\,3(NO_4)O_2$
Trigenic acid	$C_6H_7N_3O_4$	Hippuric acid	$C_{18}H_9NO_6$

Many of the organic acids which contain nitrogen are amidic acids, such as the aspartic; others are clearly substitution products, such as the carbazotic, which is a nitrous derivative of carbolic acid. Others are produced by the modification of definite compounds which contain nitrogen. Isatic acid is in this way produced from isatin:—

$$\overbrace{C_{16}H_5NO_4}^{\text{Isatin.}} + 2\,HO = \overbrace{C_{16}H_7NO_6}^{\text{Isatic Acid.}}.$$

Others are clearly compound acids, such as the hippuric, which may be regarded as a derivative of benzoic acid and glycocine. It is probable that many of the acids included in some of the foregoing groups, such as the cinnamic and coumaric, will turn out to be compound acids.

B. *Polybasic Acids.*—Amongst the polybasic acids likewise, certain homologous groups have been traced.

1. *Dibasic acids.*—Most of these acids belong to one or other of the following groups; the proportion of oxygen in the normal or hydrated acids, being 8, 10, or 12.

l.	*m.*	*n.*
1. $C_nH_nO_8$	1. $C_nH_nO_{10}$	1. $C_nH_nO_{12}$
2. $C_nH_{n-2}O_8$	2. $C_nH_{n-2}O_{10}$	2. $C_nH_{n-2}O_{12}$
3. $C_nH_{n-4}O_8$	3. $C_nH_{n-4}O_{10}$	
4. $C_nH_{n-6}O_8$	4. $C_nH_{n-6}O_{10}$	
5. $C_nH_{n-8}O_8$	5. $C_nH_{n-8}O_{10}$	
6. $C_nH_{n-10}O_8$	6. $C_nH_{n-10}O_{10}$	

One or two only of these groups have been at present clearly established: the most numerous of these is that indicated by *l.* 2, ($C_nH_{n-2}O_8$), viz.:—

Oxalic acid . .	$C_4 H_2 O_8$	Pimelic acid .	$C_{14}H_{12}O_8$
Succinic acid . .	$C_8 H_6 O_8$	Suberic acid .	$C_{16}H_{14}O_8$
Lipic acid ? , .	$C_{10}H_8 O_8$	Sebacic acid . .	$C_{20}H_{18}O_8$.
Adipic acid . .	$C_{12}H_{10}O_8$		

This group is formed by oxidation of the monobasic volatile fatty acids (*a.* 1).

To the group, *l.* 3, ($C_nH_{n-4}O_8$,) belong

Malæic and Fumaric acids . .	$C_8 H_4 O_8$
Pyrocitric acid	$C_{10}H_6 O_8$
Camphoric acid	$C_{20}H_{16}O_8$.

The only representative of the group, *l.* 4, ($C_nH_{n-6}O_8$) is

Mellitic acid	$C_8H_2O_8$.

The group *l.* 6, ($C_nH_{n-10}O_8$,) is represented by

Phthalic acid	$C_{16}H_6 O_8$
Insolinic acid	$C_{18}H_8 O_8$.

The column headed *m* in the table of dibasic formulæ, is very scantily represented; thus

m. 2, is indicated by Malic acid . . . $C_8 H_6 O_{10}$
m. 3, is indicated by Mesoxalic acid . $C_6 H_2 O_{10}$
and *m.* 5, is indicated by Comenic acid . . $C_{12}H_4O_{10}$.

The group *n.* 1, ($C_nH_nO_{12}$) has four homologous representatives, viz.;—

Glycollic acid	$C_8 H_8 O_{12}$
Lactic acid	$C_{12}H_{12}O_{12}$
Acetonic acid	$C_{16}H_{16}O_{12}$
Leucic acid	$C_{24}H_{24}O_{12}$;

and *n.* 2, ($C_nH_{n-2}O_{12}$) is represented by

Tartaric acid	$C_8H_6O_{12}$.

There are many dibasic acids which cannot be referred to any of these groups, such as

Kinic acid	$C_{28}H_{22}O_{22}$
Mucic and saccharic acids . .	$C_{12}H_{10}O_{16}$
Pyruvic acid	$C_{12}H_8 O_{12}$
Apoglucic acid	$C_{18}H_{11}O_{10}$
Uric acid	$C_{10}N_4H_4O_6$;

besides the various acids derived from the uric, by the action of oxidizing agents.

2. *Tribasic acids.*—These complicated acids do not admit of being classed in groups at present: they are comparatively few in number, the most important being the following:—

Tribasic acids.

Aconitic acid	$C_{12}H_6O_{12}$	Meconic acid	$C_{14}H_4O_{14}$
Citric acid	$C_{12}H_8O_{14}$	Chelidonic acid	$C_{14}H_4O_{12}$
Gallic acid	$C_{14}H_6O_{10}$	Glucic acid	$C_{24}H_{18}O_{18}$

(1092) *Simple, and compound or colligated acids.*—The organic acids may further be regarded as belonging to one or other of the following classes:—

a. Oxides of organic radicles, and acids derived from them by substitution.

b. Compound or *colligated* acids.

(*a*) *Oxides of Organic Radicles.*—Examples of this class occur in cyanic acid, $HO, (C_2N)O$, and in the series of volatile fatty acids (1152), the first member of which is formic acid, HO, C_2HO_3, the last as yet discovered is the melissic, $HO, C_{60}H_{59}O_3$. The fatty acids may be viewed as hydrated oxides of a compound radicle, of the form $(C_nH_{n-1}O_2)$; the radicle of formic acid being C_2HO_2, that of acetic acid $C_4H_3O_2$, and so on. These radicles, it will be observed, are oxides of hydrocarbons, in which the number of equivalents of carbon always exceeds by one that of the number of equivalents of hydrogen, a circumstance probably connected in some important manner with their acid character. Another group which falls under this subdivision, is that represented by the general formula $[HO(C_nH_{n-9}O_2)O]$, which has been characterized as the group of aromatic acids, and of which benzoic acid is the type.

(*b*) *Compound Acids.*—These acids consist of an organic compound, which may be either acid or neutral in character, united with an acid either of inorganic or organic origin, the properties of which are modified. These compound acids may be subdivided into two groups, in the first of which the saturating power of the combining acid is not affected, while in the second it is more or less diminished.

1. *Compound acids in which the capacity of saturation of the components is unchanged.*—An excellent instance of this class is afforded in the case of formobenzoylic acid $(HO, C_2HO_3 + C_{14}H_6O_2)$. This compound consists of a combination of formic acid with the oil of bitter almonds; the new acid thus formed possesses a saturating

power exactly proportioned to the quantity of formic acid which it contains. Acetonic acid ($HO, C_{16}H_{14}O_{10}$) is another example of the same kind, consisting of formic acid united with acetone ($C_6H_6O_2$) as its *colligate*, or associated organic compound.

2. *Compound acids of diminished basic power.—Sulpho-acids.* —Numerous instances of this kind occur in the colligated sulphuric acids, such as the sulphethylic ($HO, C_4H_5O, 2\,SO_3$), and sulphoglyceric acid ($HO, C_6H_7O_5, 2\,SO_3$); in these cases the sulphuric acid and the organic group in entering into combination, part with a certain number of equivalents of water; the loss of basic power in most instances corresponding to the number of equivalents of water which are displaced.

The formation of the vinic acids from the alcohols (980 *et seq.*), shows one mode in which these bodies are produced, but this series of compounds constitutes but a single subdivision of the colligated sulpho-acids, which recent researches have shown to be very numerous.

When anhydrous sulphuric acid is brought into contact with the normal or monohydrated monobasic acids, two equivalents of the anhydride generally combine with one equivalent of the organic acid, and a dibasic acid is the result. For example:—

$$\overbrace{HO,\ C_4H_3O_3}^{\text{Acetic Acid.}} + 2\,SO_3 = \overbrace{2\,HO,\ C_4H_2S_2O_8}^{\text{Sulphacetic Acid.}}.$$

The following acids belong to this class:—

Sulphacetic acid . . .	$2\,HO,\ C_4\,H_2S_2O_8$
Sulphopropionic acid . .	$2\,HO,\ C_6\,H_4S_2O_8$
Sulphobutyric acid . .	$2\,HO,\ C_8\,H_6S_2O_8$
Sulphobenzoic acid . .	$2\,HO,\ C_{14}H_4S_2O_8$.

The same compounds may be formed by heating the amides or nitriles of the series with fuming sulphuric acid. Thus, propionitrile yields sulphopropionic acid:—

$$\overbrace{C_6H_5N}^{\text{Propionitrile.}} + 2\,HO + 3\,(HO,\ SO_3) = 2\,\overbrace{HO,\ C_6H_4S_2O_8}^{\text{Sulphopropionic Acid.}} + \overbrace{H_4NO,SO_3}^{\text{Sulphate of Ammonia.}};$$

and butyramide by similar treatment furnishes sulphobutyric acid:—

$$\overbrace{C_8H_9NO_2}^{\text{Butyramide.}} + 3\,(HO,\ SO_3) = \overbrace{2\,HO,\ C_8H_6S_2O_8}^{\text{Sulphobutyric Acid.}} + \overbrace{H_4NO,SO_3}^{\text{Sulphate of Ammonia.}}.$$

But if the mixture be heated, in addition to these sulpho-acids, a second series of acids is formed, termed by Hofmann and

Buckton (*Phil. Trans.*, 1856) *disulpho-acids.* The reaction which occurs is attended with the evolution of carbonic acid; and a compound is formed which belongs to the series immediately below that of the nitrile acted upon; for example:—

$$\overbrace{C_4H_3N}^{\text{Acetonitrile.}} + 5\,(HO,\,SO_3) = \overbrace{2\,HO,\,C_2H_2S_4O_{10}}^{\text{Disulphometholic Acid.}} + 2\,CO_2 + \overbrace{H_4NO,\,SO_3}^{\text{Sulph. Ammon.}};$$

$$\overbrace{C_6H_5N}^{\text{Propionitrile.}} + 5\,(HO,\,SO_3) = \overbrace{2\,HO,\,C_4H_4S_4O_{10}}^{\text{Disulphetholic Acid.}} + 2\,CO_2 + H_4NO,\,SO_3.$$

In this manner they obtained the four first terms of the following series; and by treating aniline in a similar manner they also obtained a disulpho-acid from it. The first compound upon this list is identical with Liebig's *methionic acid;* the disulpho-naphthalic acid was discovered previously by Berzelius:—

Disulphometholic acid .	$2\,HO,\,C_2\,H_2S_4O_{10}$,	or	$C_2\,H_4,\,4\,SO_3$
Disulphetholic acid . .	$2\,HO,\,C_4\,H_4S_4O_{10}$,	or	$C_4\,H_6,\,4\,SO_3$
Disulphotritolic acid .	$2\,HO,\,C_6\,H_6S_4O_{10}$,	or	$C_6\,H_8,\,4\,SO_3$
Disulphobenzolic acid .	$2\,HO,\,C_{12}H_4S_4O_{10}$,	or	$C_{12}H_6,\,4\,SO_3$

Disulphonaphthalic acid	$2\,HO,\,C_{20}H_6S_4O_{10}$,	or	$C_{20}H_8,\,4\,SO_3$
Disulphanilic acid . .	$2\,HO,\,C_{12}H_5NS_4O_{10}$.		

Irrespective of any theoretical view of the molecular composition of the first four of these bodies, it is clear that they contain the elements of 1 equivalent of a hydrocarbon corresponding to marsh gas, with four equivalents of anhydrous sulphuric acid; as is represented in the second series of formulæ contained in the table. There can be no doubt of the possibility of forming another series of sulpho-acids corresponding to these, in which the hydrocarbon has been acted upon by two instead of by four equivalents of anhydrous sulphuric acid. These compounds would have the following composition; but at present only two of them,—viz., sulpho-benzolic and sulphanilic acid, have actually been obtained:—

Sulphometholic acid	$HO,\,C_2\,H_3S_2O_5$
Sulphetholic acid	$HO,\,C_4\,H_5S_2O_5$
Sulphotritolic acid	$HO,\,C_6\,H_7S_2O_5$
Sulphobenzolic acid	$HO,\,C_{12}H_5S_2O_5$
Sulphanilic acid	$HO,\,C_{12}H_6NS_2O_5$.

Many of these sulpho-acids may be obtained by the direct action of anhydrous sulphuric acid upon the hydrocarbons:—For example, when olefiant gas is subjected to the action of anhydrous sulphuric acid, it forms a compound which Magnus termed *sulphate of carbyle* (984); this body, when treated with water, forms ethionic or *disulphethylic* acid. This body is one of the terms of a new series of disulpho-acids, which might probably be formed by submitting the other hydrocarbons homologous with olefiant gas, to similar treatment. The ordinary vinic acids (980) constitute the series of sulpho-acids produced by the reaction of two equivalents of sulphuric acid upon the alcohol, whilst ethionic acid is one of the corresponding disulpho-acids produced by the action of 4 equivalents of sulphuric acid:—

Sulphethylic acid . . . . . $HO, C_4H_5S_2O_7$
Ethionic (disulphethylic acid) . $2\ HO, C_4H_4S_4O_{12}$

Hofmann and Buckton conclude, as the general result of their recent investigation of the sulpho-acids (*Proceedings Roy. Soc.* viii. 163)—That "all organic molecules, particularly in the nascent state, appear to be capable of assimilating the elements of either two or four equivalents of anhydrous [sulphuric] acid. The formation of the two groups of acids which are thus produced, presents a great analogy with the production of the nitro-substitutes generated under the influence of nitric acid. All these compounds are generated with the elimination of water.* In the action of nitric acid and sulphuric acid upon benzole, for instance, we have:—

$$\overbrace{C_{12}H_6}^{\text{Benzole.}} + HO, NO_5 = \overbrace{C_{12}H_5N\ O_4}^{\text{Nitrobenzole.}} + 2\ HO\ ;$$

$$C_{12}H_6 + 2\ (HO, NO_5) = \overbrace{C_{12}H_4N_2O_8}^{\text{Dinitrobenzole.}} + 4\ HO\ ;$$

$$C_{12}H_6 + 2\ HO, S_2O_6 = \overbrace{HO, C_{12}H_5S_2O_5}^{\text{Sulpho-benzolic Acid.}} + 2\ HO\ ;$$

$$C_{12}H_6 + 2\ (2\ HO, S_2O_6) = \overbrace{2\ HO, C_{12}H_4S_4O_{10}}^{\text{Disulpho-benzolic Acid.}} + 4\ HO\ .$$

The action of nitric acid upon organic bodies is by no means limited to the production of nitro-compounds corresponding to nitro-benzole and dinitro-benzole; frequently additional substitutes are formed, with elimination of six, eight, and in a few isolated cases, even of ten equivalents of water. Hitherto, however, no substances have been observed in which the assimilation of sulphuric acid has gone further than in the disulpho-acids."

Nitro-acids.—When nitric acid unites with an organic acid, the compound which is formed is generally one which is the result of a simple process of substitution. No apparent decomposition occurs in these cases, but the saturating power of the new acid is not increased by the nitrogen and oxygen which have entered into its composition. The nitric acid in reality has been partially deoxidized; an equivalent of hydrogen has been removed from the organic acid, and its place has been supplied by an equivalent of peroxide of nitrogen. For example, when benzoic acid is acted upon by nitric acid, the change which occurs is the following:—

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* This refers, however, to the case in which it is supposed that the reaction takes place between oil of vitriol or *hydrated* sulphuric acid and the organic compound, and not when the *anhydrous* acid is used; as the equations which follow sufficiently show.

$$\overbrace{HO, C_{14}H_5O_3}^{\text{Benzoic Acid.}} + HO,NO_5 = \overbrace{HO, C_{14}H_4.\, NO_4.\, O_3}^{\text{Nitrobenzoic Acid.}} + 2\,HO.$$

Many of the nitro-acids obtained in this manner are yellow, and yield salts which have a yellow colour; these salts generally fuse, and often detonate when they are exposed to heat; and when heated with sulphuric acid and peroxide of manganese they emit red nitrous fumes. A few of the best known of these compounds are enumerated below:—

Dinitrophenic acid . . .	$HO,\ C_{12}H_3\ 2\ (NO_4)\ O$
Trinitrophenic (carbazotic)	$HO,\ C_{12}H_2\ 3\ (NO_4)\ O$
Nitrobenzoic	$HO,\ C_{14}H_4\ (NO_4)\ O_3$
Dinitrobenzoic	$HO,\ C_{14}H_3\ 2\ (NO_4)\ O_3$
Nitrocinnamic	$HO,\ C_{18}H_6\ (NO_4)\ O_3$
Nitrosalicylic	$HO,\ C_{14}H_4\ (NO_4)\ O_5$
Nitranisic	$HO,\ C_{16}H_6\ (NO_4)\ O_5$.

(1093) *Action of Heat upon the Organic Acids.*—A large number of the monobasic vegetable acids, the hydrates of which contain 4 or 6 equivalents of oxygen, may be volatilized without decomposition; but the greater number of the more complicated polybasic organic acids are decomposed by the application of heat. Many of them give rise to acids of simpler composition, which are formed by the abstraction of the elements of water; or by the removal of the elements of carbonic acid; or by the loss of both water and carbonic acid. Several of these new acids are volatile; others undergo complete decomposition if subjected to a higher temperature than that at which they were formed:—For example, citric acid by losing 2 equivalents of water furnishes aconitic acid:—

$$\overbrace{3\,HO, C_{12}H_5O_{11}}^{\text{Citric Acid.}} = \overbrace{3\,HO, C_{12}H_3O_9}^{\text{Aconitic Acid.}} + 2\,HO;$$

and at a higher temperature aconitic loses carbonic acid;

$$\overbrace{3\,HO, C_{12}H_3O_9}^{\text{Aconitic Acid.}} = \overbrace{2\,HO, C_{10}H_4O_6}^{\text{Itaconic Acid.}} + 2\,CO_2.$$

The action of a gradually increasing temperature upon tartaric acid is remarkable: this acid undergoes several different stages of dehydration, and then loses carbonic acid, in the manner shown in the subjoined equations:—

$$(1)\quad \overbrace{2\,(2\,HO,\,C_8H_4O_{10})}^{\text{Tartaric Acid.}} = \overbrace{3\,HO,\,2\,(C_8H_4O_{10})}^{\text{Tartralic Acid.}} + HO\ ;$$

$$(2)\quad \overbrace{3\,HO,\,2\,(C_8H_4O_{10})}^{\text{Tartralic Acid.}} = \overbrace{2\,HO,\,2\,(C_8H_4O_{10})}^{\text{Tartrelic Acid.}} + HO\ ;$$

$$(3)\quad \overbrace{2\,HO,\,2\,(C_8H_4O_{10})}^{\text{Tartrelic Acid.}} = \overbrace{2\,(C_8H_4O_{10})}^{\text{Tartaric Anhydride.}} + 2\,HO\ ;$$

$$(4)\quad \overbrace{2\,(C_8H_4O_{10})}^{\text{Tartaric Anhydride.}} = \overbrace{2\,HO,\,C_{12}H_6O_{10}}^{\text{Pyruvic Acid.}} + 4\,CO_2\ ;$$

$$(5)\quad \overbrace{2\,HO,\,C_{12}H_6O_{10}}^{\text{Pyruvic Acid.}} = \overbrace{2\,HO,\,C_{10}H_6O_6}^{\text{Pyrotartaric Acid.}} + 2\,CO_2\ .$$

Again, malic acid, by the loss of water, yields fumaric (paramaleic) acid;

$$\overbrace{2\,HO,\,C_8H_4O_8}^{\text{Malic Acid.}} = \overbrace{2\,HO,\,C_8H_2O_6}^{\text{Fumaric Acid.}} + 2\,HO\ ;$$

and fumaric acid by sublimation is converted into its isomeride maleic acid.

In like manner gallic acid by the loss of 2 equivalents of carbonic acid yields pyrogallic acid; and pyrogallic acid in its turn, by the loss of 2 equivalents of water, furnishes metagallic acid:—

$$\overbrace{3\,HO,\,C_{14}H_3O_7}^{\text{Gallic Acid.}} = \overbrace{C_{12}H_6O_6}^{\text{Pyrogallic Acid.}} + 2\,CO_2\,;$$

$$\overbrace{C_{12}H_6O_6}^{\text{Pyrogallic Acid.}} = \overbrace{C_{12}H_4O_4}^{\text{Metagallic Acid.}} + 2\,HO.$$

Results closely analogous are afforded by the decomposition of meconic acid; a solution of which, at a temperature not exceeding that of boiling water, is converted into comenic acid by the loss of 2 equivalents of carbonic acid; and comenic acid itself if subjected to distillation loses 2 equivalents of carbonic acid, and furnishes another distinct volatile acid, the pyromeconic:—

$$\overbrace{3\,HO,\,C_{14}HO_{11}}^{\text{Meconic Acid.}} = \overbrace{2\,HO,\,C_{12}H_2O_8}^{\text{Comenic Acid.}} + 2\,CO_2\,;$$

$$\overbrace{2\,HO,\,C_{12}H_2O_8}^{\text{Comenic Acid.}} = \overbrace{HO,\,C_{10}H_3O_5}^{\text{Pyromeconic Acid.}} + 2\,CO_2.$$

(1094) *Effects of Chlorine, &c., upon the Acids.*—Chlorine generally acts upon the monobasic acids simply by displacing hydrogen, thus producing a body of the same chemical type as the original acid, and containing the same number of elements similarly arranged. In acetic acid, for instance, the 3 equivalents of hydrogen may be displaced by 3 equivalents of chlorine; and trichloracetic acid, which is analogous to the original acetic acid, is produced:—HO, $C_4H_3O_3 + 6\,Cl = HO,\,C_4Cl_3O_3 + 3\,HCl$.

By a substitution of a similar kind, benzoic acid ($HO, C_{14}H_5O_3$) yields chlorobenzoic acid $HO, C_{14}H_4ClO_3$. In other instances, especially in the more complex acids, the original group of elements is broken up into two or more groups of simpler constitution. Thus citric acid ($3\,HO, C_{12}H_5O_{11}$), when treated with chlorine, yields a neutral chlorinated body ($C_8Cl_6O_3$), besides other products. The action of bromine and of iodine is analogous to that of chlorine, but with differences depending chiefly upon the feebler character of their affinities. Peroxide of nitrogen may also be substituted for a part of the hydrogen, equivalent for equivalent; but in this case the acid character of the nitric acid whence it was derived, entirely disappears.

(1094 *bis*) It is remarkable that several of the hydrated organic acids have a composition identical with that of fructose or fruit sugar, if the ultimate analysis only be considered; thus furnishing additional evidence that chemical character depends quite as much upon the mode of arrangement among the elements, as upon the nature of those elements themselves:—

$$\overbrace{3\,(HO, C_4H_3O_3)}^{\text{3 Eqts. Acetic Acid.}} = \overbrace{2\,HO, C_{12}H_{10}O_{10}}^{\text{1 Eqt. Lactic Acid.}} = \overbrace{C_{12}H_{12}O_{12}}^{\text{1 Eqt. Fructose.}}.$$

Many of the acids contain oxygen and hydrogen in exactly the proportions required to form water: such, for example, as the lactic, the acetic, the kinic, the pyrotartaric, and some others.

(1095) *Combined Action of Heat and Bases on the Acids.*—Many of the organic acids when fused with hydrate of potash are decomposed by it into acetic and oxalic acid, with separation of water, and sometimes with evolution of hydrogen, for example:—

$$\overbrace{2\,HO, C_8H_4O_8}^{\text{Malic Acid.}} + 3\,(KO, HO) = \overbrace{2\,KO, C_4O_6}^{\text{Oxalate of Potash.}} + \overbrace{KO, C_4H_3O_3}^{\text{Acetate of Potash.}} + 4\,HO + H_2;$$

$$\overbrace{2\,HO, C_{12}H_8O_{14}}^{\text{Mucic Acid.}} + 4\,(KO, HO) = \overbrace{2\,KO, C_4O_6}^{\text{Oxalate of Potash.}} + \overbrace{2\,(KO, C_4H_3O_3)}^{\text{Acetate of Potash.}} + 8\,HO.$$

When the salts of any of the monobasic acids, which in their state of normal hydrates contain 4 equivalents of oxygen, are distilled with hydrate of baryta, they undergo a peculiar decomposition, carbonic acid is retained by the baryta, and a hydro-carbon is given off; for example:—

$$\overbrace{NaO, C_4H_3O_3}^{\text{Acetate of Soda.}} + HO, BaO = \overbrace{C_2H_4}^{\text{Marsh Gas.}} + NaO, CO_2 + BaO, CO_2;$$

$$\overbrace{CaO, C_{14}H_5O_3}^{\text{Benzoate of Lime.}} + HO, BaO = \overbrace{C_{12}H_6}^{\text{Benzole.}} + CaO, CO_2 + BaO, CO_2.$$

In this manner the salts of the following acids may be decomposed:—

Toluic acid . .	$HO, C_{16}H_7O_3$,	yielding	Toluole . .	$C_{14}H_8$
Cinnamic acid .	$HO, C_{18}H_7O_3$,	„	Cinnamole .	$C_{16}H_8$
Cuminic acid .	$HO, C_{20}H_{11}O_3$,	„	Cumole . .	$C_{18}H_{12}$

[illegible]

[illegible]

[illegible]

1096. *The Acetones or Ketones.*—When the lime or baryta salt of any of the volatile acids [illegible] hydrates of which contain 4 equivalents of oxygen, is submitted to dry distillation, the acid undergoes decomposition, and amongst the volatile products which come over, is a body which has been termed the acetone of the acid: the new body which is formed bears the same relation to the acid from which it is obtained that acetone does to acetic acid.

The general properties of this class of compounds may be illustrated by a description of acetone, which has been examined with care.

Acetone ($C_6H_6O_2$). *Sp. gr. of liquid* [illegible]; *of vapour* [illegible].—When acetate of lime is mixed with an excess of quicklime, and submitted to distillation, 2 equivalents of acetic acid lose 2 equivalents of carbonic acid, and a volatile inflammable liquid passes over, to which the formula $C_6H_6O_2$ has been assigned:—

$$\underbrace{2(CaO,\ C_4H_3O_3)}_{\text{Acetate of Lime.}} = \underbrace{2\,(CaO,\ CO_2)}_{\text{Carb. of Lime.}} + \underbrace{C_6H_6O_2}_{\text{Acetone.}}$$

When the vapours of acetic acid are transmitted through a heated porcelain tube they are resolved into acetone, carbonic acid, and water; $2\,(C_4H_4O_4) = 2\,CO_2 + 2\,HO + C_6H_6O_2$; but a better mode of preparing acetone than either of the foregoing ones consists in distilling crystallized acetate of lead, with half of its weight of quicklime.

Acetone is a colourless liquid, with an agreeable ethereal odour, and a pungent taste. It boils at 133°, and yields an inflammable vapour, which burns with a clear, white flame. When heated with hydrate of potash, it yields at a moderate temperature a mixture of acetate and formiate of potash, with liberation of hydrogen:—

$$\underbrace{C_6H_6O_2}_{\text{Acetone.}} + 2\,KO,\ HO + 2\,HO = \underbrace{KO,\ C_4H_3O_3}_{\text{Acetate of Potash.}} + \underbrace{KO,\ C_2HO_3}_{\text{Formiate of Potash.}} + 6\,H.$$

At a higher temperature carbonate of potash and marsh gas are produced:—

$$\underbrace{C_6H_6O_2}_{\text{Acetone.}} + 2\,KO,\ HO = 2\,(KO,\ CO_2) + \underbrace{2\,(C_2H_4)}_{\text{Marsh Gas.}}$$

Considerable doubt exists as to the true nature of the ketones. Kane regards acetone, which has been more thoroughly examined than any of the others, as a sort of alcohol (C_6H_5O, HO) which he has termed *mesitic alcohol;* and by distilling it with sulphuric acid he has obtained a compound having the composition C_6H_5O, which corresponds to the ether of such an alcohol; he also produced other bodies corresponding to iodide and chloride of ethyle. Acetone forms with sulphuric acid, a double acid ($2\ HO$, C_6H_5O, $2\ SO_3$). But this sulpho-acid is dibasic, unlike the true vinic acids; moreover, acetone cannot be recovered from it when it is decomposed by the hydrated alkalies; whilst all the true alcohols may be re-produced from the vinic sulpho-acids when they are decomposed in this manner by the alkalies.

Gerhardt and Chancel are disposed to consider acetone rather as a species of aldehyd, in which an equivalent of hydrogen is displaced by an equivalent of methyl;

Ethylic aldehyd $C_4H_3O_2$, H, being *hydride of othyl,*[*] and
Acetone being $C_4H_3O_2$, C_2H_3, or *methylide of othyl.*

The ketones resemble the aldehyds in their power of forming crystalline compounds with the bisulphites of potash and soda.

Any view which is adopted for acetone would be extended to the other members of this group, which are all homologous with it; thus:—

Acetone = $C_6H_6O_2$, or $C_4H_3O_2$, C_2H_3, methylide of othyl
Propione = $C_{10}H_{10}O_2$, „ $C_6H_5O_2$, C_4H_5, ethylide of propionyl
Butyrone = $C_{14}H_{14}O_2$, „ $C_8H_7O_2$, C_6H_7, tritylide of butyryl
Valerone = $C_{18}H_{18}O_2$, „ $C_{10}H_9O_2$, C_8H_9, tetrylide of valeryl.

The following results obtained by Stædeler from acetone (*Ann. de Chimie,* III. xlii. 226) have tended to confirm these views of Gerhardt and Chancel. Chlorine forms with acetone various substitution products, the most remarkable of which is one in which five equivalents of hydrogen are displaced by five of chlorine; a compound, $C_6HCl_5O_2$, analogous to chloral is thus formed; it has a sp. gr. of from 1·6 to 1·7, it is not solidified by a cold of —4°, and it boils at about 374°. This body has the property of combining with eight equivalents of water, with which it forms a soluble crystallizable substance analogous to hydrate of chloral.

Acetone when saturated with gaseous ammonia yields a liquid

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[*] Othyl is the term proposed by Williamson for the compound $C_4H_3O_2$, which Gerhardt has termed acetyl, but which must not be confounded with Liebig's acetyl, C_4H_3.

[illegible]

[illegible] has a sour taste, and is [illegible] It forms crystalline [illegible]

[illegible] with glycerine and [illegible] upon acetone, was [illegible]

It is probable that each of the other ketones would yield analogous compounds to those which Stædeler has procured from acetone. Each of the ketones is metameric with a corresponding term in the series of true aldehyds; for example:—

Acetone = $C_6 H_6 O_2$ = Propionic aldehyd.
Propione = $C_{10} H_{10} O_2$ = Valeric aldehyd.
Butyrone = $C_{14} H_{14} O_2$ = Œnanthylic aldehyd.

[illegible], Stædeler succeeded in converting acetone [illegible]

[illegible] of ketones has also been observed in the case [illegible] acids which do not belong to series of the fatty acids. Benzoic acid, for example, is decomposed in the following manner:—

$$\overbrace{2\,(\mathrm{CaO},\ C_{14}H_5O_3)}^{\text{Benzoate of Lime.}} = \overbrace{C_{26}H_{10}O_2}^{\text{Benzone.}} + \overbrace{2\,(\mathrm{CaO},\ CO_2)}^{\text{Carb. of Lime.}}\ .$$

The products of the distillation of the lime salts of the dibasic acids, such as the lactic and suberic acids, do not fall strictly into the class of ketones. The substance termed *lactone*, for instance, consists of $C_{10}H_8O_4$, instead of $C_{10}H_{10}O_6$; and *suberone* is $C_{16}H_{14}O_2$, instead of $C_{14}H_{12}O_2$.

(1097) *Oxychlorides of the Monobasic Acids.*—The acids of the lower members of the series HO, $C_nH_{n-1}O_3$, can readily be made to furnish volatile compounds in which one equivalent of oxygen, as contained in the anhydrous acid, has its place supplied by chlorine. With acetic acid (HO, $C_4H_3O_3$), an *acetic oxychloride* may be obtained, consisting of $C_4H_3O_2Cl$. In preparing these compounds Gerhardt heats together a mixture of one equivalent of the oxychloride of phosphorus* with three equivalents of the anhydrous potash or soda salt of the acid. For instance:—

$$\overbrace{3\,(\mathrm{NaO},\ C_8H_7O_3)}^{\text{Butyrate of Soda.}} + \overbrace{PO_2Cl_3}^{\text{Oxychlor. Phosph.}} = \overbrace{3\,\mathrm{NaO},\ PO_5}^{\text{Phosph. of Soda.}} + \overbrace{3\,(C_8H_7O_2Cl)}^{\text{Butyric Oxychloride.}}\ .$$

In some cases it is more advantageous to mix terchloride of phosphorus with the monohydrated acid, in the proportion of two equivalents of the acid to one equivalent of the chloride of phosphorus. In the case in which acetic acid is employed, the reaction is as follows:—

$$\overbrace{2\,(\mathrm{HO},\ C_4H_3O_3)}^{\text{Acetic Acid.}} + PCl_3 = \mathrm{HO},\ PO_3 + HCl + \overbrace{2\,(C_4H_3O_2Cl)}^{\text{Acetic Oxychloride.}}.$$

And on distilling the mixture, the new compound passes over, whilst phosphorous acid remains in the retort. By these methods the following oxychlorides have been prepared:—

Oxychlorides.	Formulæ.	Boiling point. °F.	Specific Gravity.	
			Liquid.	Vapour.
Acetic oxychloride . .	$C_4H_3O_2Cl$	131	1·125	2·87
Propionic „ . .	$C_6H_5O_2Cl$	176		
Butyric „ . .	$C_8H_7O_2Cl$	203		
Valeric „ . .	$C_{10}H_9O_2Cl$	239—248	1·005	
Pelargonic „ . .	$C_{18}H_{17}O_2Cl$	428		

One equivalent of each of these bodies yields four volumes of vapour. The vapour of these compounds is extremely irritating to the lungs, and their manipulation consequently demands great care, otherwise the health of the operator would be seriously endangered. Water immediately decomposes these oxychlorides into the hydrated acid and free hydrochloric acid. The action of a few drops of water upon acetic oxychloride is so violent as to amount to an explosion; $C_4H_3O_2Cl + 2\,HO$ becoming $HO, C_4H_3O_3 + HCl$. Oxychlorides corresponding to the foregoing compounds may also be obtained with the aromatic acids, such as the benzoic, cinnamic, and cuminic acids.

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* Gerhardt has given an easy method of procuring oxychloride of phosphorus for these decompositions. It consists in distilling 5 parts of perchloride of phosphorus with rather more than 1 part of crystallized boracic acid, when the following reaction occurs; $3PCl_5+2(3HO,BO_3)=3PO_2Cl_3+6\,HCl+2BO_3$.

Oxychlorides.	Formulæ.	Boiling point. °F.	Specific Gravity.	
			Liquid.	Vapour.
Benzoic oxychloride .	$C_{14}H_5\,O_2Cl$	385	1·25	4·987
Cinnamic	$C_{18}H_7\,O_2Cl$	502	1·207	
Cuminic	$C_{20}H_{11}O_2Cl$	495	1·070	
Anisic	$C_{16}H_7\,O_4Cl$	504	1·261	

(Cahours, *Ann. de Chimie,* III. xxiii. 337).

These oxychlorides, though unimportant in themselves, have in the hands of Gerhardt, led to the unexpected discovery of a general method of procuring the anhydrides of the acids from which they are derived (1099). If oxybromide of phosphorus be used instead of the oxychloride for decomposing the salt of the organic acid, oxybromides of corresponding composition may be procured.

(1098) *Oxychlorides of the dibasic acids,* such as the succinic oxychloride ($C_8H_4O_4Cl_2$), and citraconic oxychloride ($C_{10}H_4O_4Cl_2$), may also be procured, but it is best in these cases to act upon the anhydrides of these acids with the perchloride of phosphorus: they are obtained in a state of purity with difficulty, since they are generally decomposed at a temperature below their point of volatilization.

(1099) *The Anhydrides, or Anhydrous Acids.*—The oxychlorides of the monobasic acids may be employed to furnish the anhydrides of their respective acids, by causing an equivalent of the oxychloride to decompose an equivalent of the dry potash or soda salt of the acid to which it corresponds. For instance, in the preparation of acetic anhydride, an equivalent of acetic oxychloride is treated with an equivalent of anhydrous acetate of potash, when the following reaction occurs:—

$$\overbrace{C_4H_3O_2Cl}^{\text{Acetic Oxychloride.}} + \overbrace{KO,\,C_4H_3O_3}^{\text{Acetate of Potash.}} = KCl + \overbrace{C_4H_3O_3,\,C_4H_3O_3}^{\text{Acetic Anhydride.}}.$$

The oxychloride of phosphorus is condensed readily, whilst the hydrochloric acid passes off in the form of gas, and anhydrous boracic acid is left in the retort. Oxalic acid may be substituted for boracic acid in this operation, but it does not answer quite so well.

It is not necessary to isolate the oxychloride in order to procure the anhydride of the acid, for if one equivalent of oxychloride of phosphorus be made to act upon six equivalents of the anhydrous salt, instead of upon three equivalents, as would be required in the preparation of the oxychloride of the organic acid, a compound reaction occurs. The oxychloride of the acid is first formed, and this body in the moment of its formation reacts upon the excess of the salt employed, and the anhydride is at once liberated. For example, in the preparation of acetic anhydride, these two stages would be thus indicated:—

$$\text{(1)}\quad \overbrace{PO_2Cl_3}^{\text{Oxychlor. Phosph.}} + \overbrace{3\,(KO,\,C_4H_3O_3)}^{\text{Acetate of Potash.}} = 3\,KO,\,PO_5 + \overbrace{3\,(C_4H_3O_2Cl))}^{\text{Acetic Oxychloride.}};$$

$$\text{(2)}\quad \overbrace{3\,(C_4H_3O_2Cl)}^{\text{Acetic Oxychloride.}} + \overbrace{3\,(KO,\,C_4H_3O_3)}^{\text{Acetate of Potash.}} = 3\,KCl + \overbrace{3\,(C_4H_3O_3,\,C_4H_3O_3)}^{\text{Acetic Anhydride.}}.$$

Or the whole may be comprehended in a single equation such as the following, which represents the preparation of valeric anhydride:—

$$\overbrace{PO_2Cl_3}^{\text{Oxychl. Phosph.}} + 6\overbrace{(KO,\,C_{10}H_9O_3)}^{\text{Valerate of Potash.}} = 3\,KO,\,PO_5 + 3\,KCl + 3\overbrace{(C_{10}H_9O_3,\,C_{10}H_9O_3)}^{\text{Valeric Anhydride.}}.$$

Gerhardt and Chiozza have thus obtained the anhydrides of the following acids:—

Anhydrides.	Formulæ.	Boiling Point ° F.	Specific Gravity.	
			Liquid.	Vapour.
Acetic . . .	$(C_4H_3O_3,\ C_4H_3O_3)$	280	1·073	3·47
Butyric . . .	$(C_8H_7O_3,\ C_8H_7O_3)$	374	0·978	5·38
Valeric . . .	$(C_{10}H_9O_3,\ C_{10}H_9O_3)$	419	0·934	6·23
Caproic . . .	$(C_{12}H_{11}O_3,\ C_{12}H_{11}O_3)$			
Œnanthylic . .	$(C_{14}H_{13}O_3,\ C_{14}H_{13}O_3)$		0·92	
Caprylic . . .	$(C_{16}H_{15}O_3,\ C_{16}H_{15}O_3)$	about 536		
Pelargonic . .	$(C_{18}H_{17}O_3,\ C_{18}H_{17}O_3)$			

These anhydrides assume the form of neutral oily bodies, which are insoluble in water, but which by contact with this liquid are gradually converted into the corresponding hydrated acids. They are susceptible of volatilization without undergoing decomposition. They possess, in many cases, an odour distinct from that of the hydrated acids to which they give rise. In entering into combination with ammonia, they form amides or salts of amidated acids (1047).

But the mode in which these compounds are formed is of greater interest to chemical theory than the mere fact of their existence. They are formed, it will be observed, not by the abstraction of water from the hydrated acids, nor by the removal of a metallic oxide from one of the salts of the acid, but by a true process of substitution, so that the anhydrides of these monobasic acids cannot be accurately represented by any formula which would indicate that they consisted of a salt deprived of its base, or of a hydrate deprived of its water. For example, acetic acid in its most concentrated form, is represented as $HO, C_4H_3O_3$, and acetate of potash is $KO, C_4H_3O_3$, but acetic anhydride is not simply $C_4H_3O_3$. It is truly $C_4H_3O_3, C_4H_3O_3$, since it is formed by substituting an equivalent of $C_4H_3O_2$, in the place of an equivalent of hydrogen or of potassium :—

$$\overbrace{(KO, C_4H_3O_3)}^{\text{Acetate of Potash.}} + \overbrace{(C_4H_3O_2)Cl}^{\text{Acetic Oxychloride.}} = KCl + \overbrace{(C_4H_3O_3, C_4H_3O_3)}^{\text{Acetic Anhydride.}}.$$

The normal (1168) specific gravity of the vapour of monohydrated acetic acid (at 482° F.) is 2·080; that is to say, 1 equivalent yields 4 volumes of vapour: the density of the anhydride is 3·47,—consequently its equivalent (supposing it to yield 4 volumes of vapour) must be represented by the formula $(C_4H_3O_3, C_4H_3O_3)$. But the following proof of the correctness of the theory of this duplicate composition of the anhydrides, will, perhaps, by many be esteemed still more convincing.

(1100) *Double Anhydrides.*—The anhydrides already enumerated are not the only ones which Gerhardt has succeeded in obtaining. Benzoic, cinnamic, and cuminic oxychlorides may be procured, by processes analogous to those already described for the preparation of the acetic and other oxychlorides; and the corresponding anhydrides were obtained by employing these oxychlorides to decompose the anhydrous salts of benzoic, cinnamic, and cuminic acids :—

	Oxychlorides.	Anhydrides.
Benzoic	$C_{14}H_5O_2Cl$	$(C_{14}H_5O_3, C_{14}H_5O_3)$
Cinnamic	$C_{18}H_7O_2Cl$	$(C_{18}H_7O_3, C_{18}H_7O_3)$
Cuminic	$C_{20}H_{11}O_2Cl$	$(C_{20}H_{11}O_3, C_{20}H_{11}O_3)$
Nitrobenzoic	$C_{14}\left.\begin{matrix}H_4\\NO_4\end{matrix}\right\\} O_2Cl$	$(C_{14}\left.\begin{matrix}H_4\\NO_4\end{matrix}\right\\} O_3, C_{14}\left.\begin{matrix}H_4\\NO_4\end{matrix}\right\\} O_3)$
Salicylic	$C_{14}H_5O_4Cl$	$(C_{14}H_5O_5, C_{14}H_5O_5)$

Gerhardt, however, did not stop here; he employed the oxychlorides already described, to decompose the salts of *other* acids. Thus benzoic oxychloride was made to decompose dry cuminate of soda, and in this manner a *benzo-cuminic* anhydride was obtained by the following reaction :—

$$\overbrace{C_{14}H_5O_2Cl}^{\text{Benzoic Oxychloride.}} + \overbrace{NaO, C_{20}H_{11}O_3}^{\text{Cuminate of Soda.}} = NaCl + \overbrace{(C_{14}H_5O_3, C_{20}H_{11}O_3)}^{\text{Benzo-cuminic Anhydride.}}.$$

By decomposing cinnamate of soda by benzoic oxychloride, *benzo-cinnamic* anhydride was obtained: and by similar methods the various compounds enumerated in the following list were procured :—

Benzo-cuminic anhydride	$C_{14}H_5O_3, C_{20}H_{11}O_3$
Benzo-cinnamic anhydride	$C_{14}H_5O_3, C_{18}H_7O_3$
Benzo-benzoic anhydride	$C_{14}H_5O_3, C_{14}H_5O_3$
Benzo-acetic anhydride	$C_{14}H_5O_3, C_4H_3O_3$
Cinnamo-acetic anhydride	$C_{18}H_7O_3, C_4H_3O_3$
Benzo-nitro-benzoic anhydride	$C_{14}H_5O_3, C_{14}\left.\begin{matrix}H_4\\NO_4\end{matrix}\right\}O_3$
Benzo-salicylic anhydride	$C_{14}H_5O_3, C_{14}H_5O_5$
Aceto-salicylic anhydride	$C_4H_3O_3, C_{14}H_5O_5$
Benzo-valeric anhydride	$C_{14}H_5O_3, C_{10}H_9O_3$

These compounds are liquid at ordinary temperatures, and assume the form of neutral oils, which are heavier than water; if left in contact with water they are gradually converted into a mixture of the two monohydrated acids from which they are derived; benzo-acetic anhydride, for instance, combining with two equivalents of water, and forming a mixture of normal benzoic and acetic acids. If it be attempted to submit these double anhydrides to distillation, they become decomposed, and are generally resolved into their component anhydrides. It is obvious that the foregoing list might be increased almost indefinitely, were there any inducement to add to the number of these compounds; intrinsically they are unimportant, but the interesting point which is indicated by their discovery, is the fact that the anhydrides of the monobasic acids are really complex bodies, resulting from the combination of two substances of similar composition: the true benzoic anhydride, or benzo-benzoic compound, which stands third upon the foregoing list, being perfectly analogous, not only in its mode of formation, but also in its properties, to the other bodies with which it is associated; it is, however, more stable than they are, and can be distilled without experiencing decomposition.

(1101) *Anhydrides of the Dibasic Acids.*—With the dibasic acids the case is different. The anhydrides of these compounds can often be obtained from the hydrated acids, by the simple application of heat to these bodies, or by distilling them with dehydrating agents, such as anhydrous phosphoric acid. In this manner, for instance, chemists have been enabled to procure the following anhydrides of dibasic acids :—

Succinic anhydride	$C_8H_4O_6$	Citraconic . . .	$C_{10}H_4O_6$
Malæic	$C_8H_2O_6$	Lactic	$C_{12}H_{10}O_{10}$
Tartaric . . .	$C_8H_4O_{10}$	Phthalic . . .	$C_{16}H_4O_6$
Pyrotartaric . .	$C_{10}H_6O_6$	Camphoric . . .	$C_{20}H_{14}O_8$

These being residues of dibasic acids are already *double* anhydrides, and it will be observed that in every case the number of equivalents of each element is divisible by two. Succinic anhydride, for instance, may still be represented as formed upon the type of the double atom of water $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$, thus $\left.\begin{matrix}C_4H_2O_2\\C_4H_2O_2\end{matrix}\right\}O_2$; and the same may be said of tartaric anhydride $\left.\begin{matrix}C_4H_2O_4\\C_4H_2O_4\end{matrix}\right\}O_2$, and indeed of all the others.

It is worthy of remark, that these dibasic acids are the only acids which form vinic or ethylic acids, such as sulphethylic, oxalethylic, and tartrethylic: and it is they only that can furnish the amidated acids, such as the oxamic, tartramic, and lactamic acids.*

If instead of causing an oxychloride of a monobasic acid to act upon one of the salts of another monobasic acid (as when benzoic oxychloride (chloride of benzoyl) is made to act upon dry acetate of potash), the oxychloride be made to act upon the corresponding salt of a dibasic acid, a double anhydride is not formed, but a mixture of two separate anhydrides is the result. Thus, if benzoic oxychloride be made to act upon dry succinate of soda, a mixture of succinic and benzoic anhydrides is obtained. This result may be explained as follows:—

Each equivalent of the salt of a dibasic acid contains within itself two equivalents of a metallic oxide, in addition to the elements of the corresponding anhydride; there are consequently two stages in the reaction. In the first of these stages the oxychloride decomposes the salt into the anhydrous acid, and into a new salt of the monobasic acid corresponding to the oxychloride used; and in the second stage, this newly formed salt is in its turn decomposed by an additional quantity of the oxychloride, as in the case of the monobasic salts where this latter reaction is the only one which occurs.† For example:—

$$\text{1st stage; } \overbrace{C_{14}H_5O_2Cl}^{\text{Benzoic Oxychloride.}} + \overbrace{2\,NaO,C_8H_4O_6}^{\text{Succinate of Soda.}} = \overbrace{C_8H_4O_6}^{\text{Succinic Anhydride.}} + NaCl + \overbrace{NaO,C_{14}H_5O_3}^{\text{Benzoate of Soda.}};$$

$$\text{2nd stage; } \overbrace{C_{14}H_5O_2Cl}^{\text{Benzoic Oxychloride.}} + \overbrace{NaO,\ C_{14}H_5O_3}^{\text{Benzoate of Soda.}} = \overbrace{C_{14}H_5O_3,\ C_{14}H_5O_3}^{\text{Benzoic Anhydride.}} + NaCl.$$

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* The compound improperly called benzamic acid ($HO,\ C_{14}H_6NO_3$) is not an amidated acid at all (1209), and therefore is no exception to this rule.

† Upon Gerhardt's theory, the sole difference between the anhydrides of the dibasic and the monobasic acids, (for example, between succinic and acetic

The action of perchloride of phosphorus upon the hydrated acids affords a means of distinguishing between the dibasic and the monobasic acids. In both cases the oxychloride of the acid is formed, but in the case of the dibasic acids the reaction occurs in two stages, in the first of which the anhydride of the acid is produced, whilst in the second stage this anhydride passes into the oxychloride; but with the monobasic acids there is only one stage: hydrated succinic acid, for example, thus yields in the first place anhydrous succinic acid, hydrochloric acid, and oxychloride of phosphorus; and in the second stage of the reaction with an additional quantity of the perchloride of phosphorus, oxychloride of phosphorus, and succinic oxychloride, are formed:—

$$\text{1st stage; } \overbrace{2\,HO,\,C_8H_4O_6}^{\text{Succinic Acid.}} + \overbrace{PCl_2Cl_3}^{\substack{\text{Perchlor.}\\ \text{Phosph.}}} = \overbrace{C_8H_4O_6}^{\substack{\text{Succinic}\\ \text{Anhydride.}}} + \overbrace{PO_2Cl_3}^{\substack{\text{Oxychlor.}\\ \text{Phosph.}}} + 2\,HCl;$$

$$\text{2nd stage; } \overbrace{C_8H_4O_6}^{\text{Succinic Anhydride.}} + PCl_2Cl_3 = \overbrace{C_8H_4O_4Cl_2}^{\text{Succinic Oxychloride.}} + PO_2Cl_3.$$

Perchloride of phosphorus never yields the anhydride of a monobasic acid by acting upon the hydrated acid; but the corresponding oxychloride is formed at once, whilst oxychloride of phosphorus and hydrochloric acid are liberated. Thus:—

$$\overbrace{HO,\,C_4H_3O_3}^{\text{Acetic Acid.}} + PCl_2Cl_3 = \overbrace{C_4H_3O_2Cl}^{\text{Acetic Oxychloride.}} + HCl + PO_2Cl_3$$

(1102) *Gerhardt's Theory of the composition of the Monobasic and Dibasic Acids.*—The important experiments which have just been detailed, have given great additional probability to a theory of the constitution of organic compounds, long advocated by Laurent and Gerhardt, and which we shall briefly explain in its application to the monobasic and dibasic acids. The basis of this remarkable theory is, that the *normal acids*, or hydrated acids as they are usually termed, are formed upon the type of the molecule of water, which molecule is supposed to consist of $\left.\begin{matrix}H\\H\end{matrix}\right\}O$: the equivalent of oxygen

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anhydrides, supposing them both to be compared with the molecule of water taken as $\left.\begin{matrix}H\\H\end{matrix}\right\}O$), is, that the two molecules of hydrogen assumed by Gerhardt to exist in the molecule of water, are displaced in the dibasic anhydride by a single indivisible group (such as $C_4H_4O_2 = C_8H_4O_4$), whilst in the monobasic anhydride this displacement is effected by two identical groups, (such as $C_2H_3O = C_4H_3O_2$), which need not coexist in the compound, but one of which can be exchanged for another similar or corresponding group. (See also § 1102.)

being double of that generally admitted.* It is assumed that hydrogen is incapable of existing in a separate form, except in the condition of the double atom $\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}$. This double atom, however, is divisible when in combination; the divisibility being evidenced by the circumstance that one atom (H) admits of being displaced by an atom of some other body, or group of bodies, which represents hydrogen when in combination. In the hydrated monobasic acids, such a substitution is supposed to have occurred; acetic hydrate (monohydrated acetic acid) being represented as $\left.\begin{matrix}C_2\mathrm{H}_3O\\\mathrm{H}\end{matrix}\right\}O$; the group $C_2\mathrm{H}_3O$ occupying the place of one of the molecules of hydrogen in the atom of water. If the place of the second molecule of hydrogen in the typical atom of water be occupied by a metal, a *salt* of the acid is formed; thus, acetate of potash would be $\left.\begin{matrix}C_2\mathrm{H}_3O\\\mathrm{K}\end{matrix}\right\}O$; in which a molecule of potassium has been substituted for the second molecule of hydrogen. Further, if the second equivalent of hydrogen be displaced by a second group, similar to that which occupies the place of the first, the *anhydride* of the acid is obtained; thus acetic anhydride would be $\left.\begin{matrix}C_2\mathrm{H}_3O\\C_2\mathrm{H}_3O\end{matrix}\right\}O$; in which the position of both the molecules of hydrogen in the typical atom of water, is occupied by the group $C_2\mathrm{H}_3O$.

The normal hydrates of the dibasic acids are supposed to have a different constitution; for in them a single indivisible group of atoms is considered to be combined with a molecule of water; succinic hydrate, for instance, being $\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}O,\ C_4\mathrm{H}_4O_2,O$. When one of the molecules of the hydrogen contained in the basic molecule of water is displaced by a single equivalent of a metal, an acid salt is formed: acid succinate of soda, for instance, being $\left.\begin{matrix}\mathrm{Na}\\\mathrm{H}\end{matrix}\right\}O,\ C_4\mathrm{H}_4O_2,\ O$; and when the second molecule of hydrogen is displaced by a second equivalent of a metal, a neutral salt of the dibasic acid is produced; succinate of potash and magnesia, for instance, being $\left.\begin{matrix}\mathrm{K}\\\mathrm{Mg}\end{matrix}\right\}O,\ C_4\mathrm{H}_4O_2,\ O$. Further, when the molecule of water is abstracted altogether, the anhydride of the acid is left:—succinic anhydride thus consists simply of the hydrated acid deprived of its molecule of basic water; $\left.\begin{matrix}H\\H\end{matrix}\right\}O, C_4H_4O_2, O,$ becoming separated into $\left.\begin{matrix}H\\H\end{matrix}\right\}O,$ and $C_4H_4O_2,O$.

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* Gerhardt's double equivalents of oxygen, carbon, and sulphur, are here, as elsewhere, represented in italic capitals; thus, $O = 16$, $C = 12$, $S = 32$.

This theory has the merit of accounting for the necessity of forming the anhydrides of the monobasic acids by substitution; whilst it also explains the possibility of procuring the anhydrides of the dibasic acids by simple dehydration.

In order that a clearer idea may be obtained of the difference between Gerhardt's view and the one usually adopted by chemists, we subjoin an example of the application of the formulæ of both theories to acetic acid, which has been selected as the type of a monobasic acid; and to succinic acid, which may serve as the type of a dibasic acid.*

Monobasic Acid.	Ordinary View.	Gerhardt.
Hydric Acetate, or Hydrated Acetic Acid	$HO, C_4H_3O_3$	$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$
Potassic Acetate, or Acetate of Potash	$KO, C_4H_3O_3$	$\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O$
Acetic Acetate, or Anhydrous Acetic Acid	$C_4H_3O_3, C_4H_3O_3$	$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O$

Dibasic Acid.	Ordinary View.	Gerhardt.
Succinic Hydrate, or Hydrated Succinic Acid	$2HO, C_8H_4O_6$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O, C_4H_4O_2, O$
Acid Succinate of Soda	$NaO, HO, C_8H_4O_6$	$\left.\begin{matrix}H\\Na\end{matrix}\right\}O, C_4H_4O_2, O$
Neutral Succinate of Soda	$2NaO, C_8H_4O_6$	$\left.\begin{matrix}Na\\Na\end{matrix}\right\}O, C_4H_4O_2, O$
Double Succinate of Magnesia and Potash	$KO, MgO, C_8H_4O_6$	$\left.\begin{matrix}K\\Mg\end{matrix}\right\}O, C_4H_4O_2, O$
Succinic Anhydride . . .	$C_8H_4O_6$	$C_4H_4O_2, O$

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* Although acetic acid, and the acids of the series to which it belongs are regarded as monobasic, it must not be forgotten that a large number of these acids form acid salts with potash, such as biformiate, binacetate, and bistearate of potash. No satisfactory explanation of the occurrence of these salts is afforded on the supposition that these acids are monobasic. The exact distinction between a monobasic and dibasic acid, therefore, still requires further researches for its elucidation.

and is soluble in alcohol and in ether: if heated gradually in vessels from which air is excluded, it may be distilled, though partial decomposition is apt to occur, unless the heat be carefully regulated. When exposed to a long-continued heat of about 266° F. the acid gradually loses water, and is converted into $C_{12}H_{10}O_{10}$, or *lactic anhydride*, which is a yellowish, fusible bitter substance, nearly insoluble in water, but soluble in alcohol and in ether: by long contact with cold water, it is converted into ordinary lactic acid: the same change takes place, more quickly, if it be boiled with water.

If lactic acid be heated to about 500° F. decomposition ensues; carbonic acid and aldehyd are formed; while a volatile acid, the citraconic, and a body termed *lactide* distil over. The relation of aldehyd to lactic acid is readily traced:—

$$\overbrace{2\,HO,\,C_{12}H_{10}O_{10}}^{\text{Lactic Acid.}} = 4\,HO + 4\,CO + \overbrace{2\,(C_4H_4O_2)}^{\text{Aldehyd.}}.$$

Aldehyd admits of being reconverted into lactic acid, as will be explained when speaking of alanine.

Pelouze also obtained during the distillation of lactic acid, a volatile liquid, to which he gave the name of *lactone* ($C_{10}H_8O_4$): it has a pungent odour, and boils at about 198°.

Lactide contains ($C_{12}H_8O_8$), the elements of anhydrous lactic acid, minus 2 equivalents of water: it is dissolved freely by boiling absolute alcohol, and crystallizes from it on cooling in brilliant rhombic prisms; at 225° it fuses, and at a higher temperature it may be sublimed unchanged. Water dissolves it slowly but completely, but it cannot be crystallized from this solution, since it passes at once into hydrated lactic acid, by assuming 4 equivalents of water. Lactide readily absorbs ammonia, and is converted into lactamide; $C_{12}H_8O_8 + 2\,H_3N = 2\,(H_2N)C_{12}H_{10}O_8$; this body is isomeric with sarcosine, and with alanine.

Lactates.—The lactic is a dibasic acid: the lactates are soluble in water, but insoluble in ether, and nearly so in cold alcohol: those of the alkalies do not crystallize. Neutral and acid lactates may be formed with lime and with baryta. *Bilactate of baryta* ($BaO,\ HO,\ C_{12}H_{10}O_{10}$) may be crystallized: the neutral lactate is very soluble in water, and does not crystallize. *Acid lactate of lime* ($CaO,\ HO,\ C_{12}H_{10}O_{10},\ 2\,Aq$) crystallizes in radiated needles. *Neutral lactate of lime* crystallizes in tufts of prisms, with 10 equivalents of water. The *lactate of zinc*, $2\,ZnO,\ C_{12}H_{10}O_{10},\ 6\,Aq$, is one of the most characteristic salts of this acid; it crystallizes in crusts, consisting of four-sided prisms, which are sparingly soluble.

Lactate of copper ($CuO, C_{12}H_{10}O_{10}$ 4 Aq) is only incompletely precipitated by hydrate of potash, an excess of which gives with it a deep blue solution; but the whole of the oxide of copper is separated on the addition of an excess of hydrate of lime. A *sublactate* of copper ($4 CuO, C_{12}H_{10}O_{10}$) may also be obtained. Several other basic lactates may be formed, which, like sublactate of copper, contain 4 equivalents of base.

The variety of lactic acid which is obtained from the juice of flesh, yields salts which crystallize with a proportion of water differing from that contained in the salts furnished by the ordinary acid. The acid obtained from muscular tissue, may be distinguished as the variety α; its salts crystallize with smaller proportions of water of crystallization than those of the ordinary form of the acid, which may be distinguished as the variety β; thus it gives a salt of zinc, which contains only 4 equivalents of water, and crystallizes in slender needles; it begins to undergo decomposition below 300°, whilst the salt of the ordinary acid may be heated to 400° without experiencing any decomposition. The neutral salt of lime, of the variety α, also crystallizes with 8 equivalents of water, and is less soluble than the variety β, which crystallizes with 10 Aq. Similar differences are observed in the copper salts; but the copper salt α is much the more soluble of the two.

Lactic acid coagulates albumen; when present in small quantity it does not curdle milk in the cold, but does so if gently heated.

The lactates, when heated with sulphuric acid, give off pure carbonic oxide, and deposit a solid brown matter resembling ulmic acid. By nitric acid the lactic is converted into oxalic acid.

The tests for lactic acid are not very definite. The best mode of identifying it (whether it be free or in combination), consists in evaporating the liquid suspected to contain it, to the consistence of a syrup over a water bath, treating the residue with alcohol, and adding a small quantity of a solution of oxalic acid: the bases are thus separated in combination with the oxalic acid; but the lactic acid, and the excess of oxalic acid, remain dissolved. The acid liquid is carefully neutralized by baryta water, which causes a precipitate of oxalate of baryta; whilst the lactate of this base remains dissolved. The lactate of baryta may be decomposed by adding a solution of sulphate of lime; sulphate of baryta is thus separated, and the lactate of lime may be crystallized from the alcoholic solution, and the form of the crystals ascertained by the microscope.

Lactic acid is largely produced in the animal body; besides forming an unfailing constituent of the fluids of the muscular tissue, it is one of the acids contained in the gastric juice, and in cases of diabetes it has been found, by Lehmann, in the saliva. It has also been met with in the urine, but it is not one of the normal constituents of this excretion: it has likewise been frequently found in the sweat.

Lactic acid appears to belong to a group of homologous dibasic acids, consisting of the following members:—

Glycolic acid	$2\ HO, C_8H_6O_{10}$
Lactic acid	$2\ HO, C_{12}H_{10}O_{10}$
Acetonic acid	$2\ HO, C_{16}H_{14}O_{10}$
Leucic acid	$2\ HO, C_{24}H_{22}O_{10}$

2. *Tartaric Acid, and its Derivatives.*

(1105) *Isomeric forms of Tartaric Acid.*—The remarkable researches of Pasteur (*Ann. de Chimie,* III. xxiv. 442, and xxviii. 56) upon the optical and chemical properties of tartaric acid, have opened a new and important method of investigating the molecular composition of organic bodies. He has proved the existence of two varieties of tartaric acid, which may be distinguished by the peculiarities of their crystals. The crystals of each variety of tartaric acid are always unsymmetrical; but the deficit in symmetry displayed by the crystals of one variety, is exactly the reverse of that manifested by those of the other variety. Each of these forms of tartaric acid exerts a powerful effect of rotation upon a ray of polarized light; but the effect produced by equal quantities of the two varieties of the acid, though equal in amount, is opposite in direction. One of the modifications exhibits a crystalline form, which is termed *dextro-hemihedral*; its solution produces right-handed rotation of a ray of polarized light: this variety is known as *dextro-tartaric,* or *dextro-racemic acid*: it is the usual form of the acid. The other modification is *lævo-hemihedral,* and produces a left-handed rotation of a polarized ray: this modification constitutes *lævo-tartaric,* or *lævo-racemic acid.* The two acids are so related in crystalline form, that if a salt of the acid which is dextro-hemihedral be held before a mirror, the reflection of the crystal will exactly represent the form of the corresponding crystal of the lævo-hemihedral acid. Both these modifications are exactly similar in chemical properties, so long as they are combined with bodies which exert no action upon polarized light; but this identity in chemical properties disappears when they are united with bodies endowed with rotatory power upon polarized light: for example, dextro-tartaric acid forms with asparagin a crystalline compound, whilst the lævo-tartaric acid forms with this body a gummy mass.

When concentrated solutions of equal parts of dextro-tartaric and of lævo-tartaric acids are mixed together, the temperature rises considerably: and on cooling, crystals of a different acid are formed. This new acid is identical with the *paratartaric* or *racemic acid*: it has no longer the power of causing the rotation of a ray of polarized light, and it presents differences in its chemical reactions (1109) from those of either of its components.

Yet, if the acid thus obtained be divided into two equal parts, one-half being neutralized with soda, then mixed with the other half of the acid and neutralized with ammonia, the solution on evaporation will yield crystals, each of which has a powerful rotatory action on polarized light; but the crystalline mass will be found to consist of a mixture of the right-handed and of the left-handed double tartrate of soda and ammonia, in equal proportions. The crystals of the two salts are recognised by their opposite hemihedral form, and may be separated by hand. If all the right-handed crystals be dissolved separately in water, and decomposed by adding a solution of nitrate of lead, a precipitate consisting of the dextro-tartrate of lead will be deposited. From this precipitate the dextro-tartaric acid may be separated by means of sulphuric acid, and may be obtained in crystals on evaporation: if the lævo-hemihedral crystals be treated in a similar manner, lævo-tartaric acid may also be procured.

It was by treating the natural racemate of soda of ammonia in this manner, and picking out each crystal separately, that Pasteur was enabled to prove the existence of the two modifications of tartaric acid, and to show that racemic acid consists of a mixture of two acids which exert opposite effects of rotation on polarized light.

Very few of the salts of racemic acid thus spontaneously separate into the two different hemihedral varieties of crystalline form; the racemate of cinchonicine (1074) is easily separable into its component crystals, and the racemate of quinicine also exhibits a similar property. These salts may therefore be employed for the purpose of isolating the two modifications of tartaric acid, when they occur in combination: at a certain stage of concentration of the racemate of cinchonicine, the first crop of crystals consists chiefly of the lævo-tartrate. When racemate of quinicine is employed, the crystals which are first deposited consist mainly of the dextro-tartrate.

(1106) Ordinary Tartaric Acid, or *Dextroracemic Acid* ($2HO, C_8H_4O_{10}$).—The principal supply of this acid is obtained from the grape; but it is also present in the tamarind and in the unripe berries of the mountain ash: it is likewise frequently met with in small quantity in other plants. Grape juice contains it in the form of bitartrate, or as it is sometimes called, supertartrate of potash, constituting the crust or tartar which is deposited in the vessel in which the wine is kept.

Preparation.—In order to prepare the acid, crude tartar is dissolved in boiling water, and chalk is added so long as effervescence occurs, 4 parts of tartar requiring about 1 part of chalk; an insoluble tartrate of lime is thus precipitated, and neutral tartrate of potash remains dissolved. Tartaric acid being dibasic, the change which occurs may be thus represented:—Two equivalents of bitartrate of potash react upon two equivalents of carbonate of lime, and form one equivalent of dibasic neutral tartrate of lime, and one of dibasic neutral tartrate of potash; thus:—

$$2\,\overbrace{(KO, HO, C_8H_4O_{10})}^{\text{Bitartrate of Potash.}} \quad + \quad 2\,\overbrace{(CaO, CO_2)}^{\text{Carbonate of Lime.}} \text{ yield}$$

$$2\,\overbrace{CaO, C_8H_4O_{10}}^{\text{Tartrate of Lime.}} \quad + \quad 2\,\overbrace{KO, C_8H_4O_{10}}^{\text{Tartrate of Potash.}}\ .$$

The tartrate of potash in solution may be decomposed by the addition of an equivalent quantity of chloride of calcium, and the whole of the tartaric acid may thus be separated as tartrate of lime.

$$2\,\overbrace{KO, C_8H_4O_{10}}^{\text{Tartrate of Potash.}} \ + \ 2\,CaCl \ = \ 2\,KCl \ + \ 2\,\overbrace{CaO, C_8H_4O_{10}}^{\text{Tartrate of Lime.}}\ .$$

The product of the two operations is well washed, and digested with oil of vitriol diluted with 6 or 8 times its weight of water: for every 5 parts of tartar 3 parts of concentrated sulphuric acid are required; the solution is allowed to digest at a gentle heat, sulphate of lime is formed, and tartaric acid set free. When cool, the liquid is filtered, evaporated in leaden vessels to the consistence of syrup, and allowed to crystallize; the formation of crystals is favoured by the presence of an excess of sulphuric acid.

Properties.—The acid thus obtained assumes the form of oblique rhombic prisms; when pure they are colourless, transparent, and permanent in the air. Tartaric acid is very soluble in water, in alcohol, and in wood spirit; it has a sharp agreeable acid taste. If heated with the caustic alkalies water is expelled, and oxalate and acetate of the base are formed—

$$\overbrace{2HO, C_8H_4O_{10}}^{\text{Tartaric Acid.}} + 3\,(KO, HO) = \overbrace{KO, C_4H_3O_3}^{\text{Acetate of Potash.}} + 2\,\overbrace{KO, C_4O_6}^{\text{Oxalate of Potash.}} + 6\,HO.$$

Its aqueous solution becomes mouldy when long kept, and is slowly converted into acetic acid.

The crystals of tartaric acid, when gently heated, become as strongly electrical as those of tourmaline. Its solutions, particularly when hot, exert a powerful right-handed rotation upon a ray of polarized light. When tartaric is boiled with nitric acid, oxalic acid is formed, together with an acid homologous with the malic. Tartaric acid exhibits considerable tendency to combine with oxygen. If it be boiled with peroxide of lead it undergoes decomposition, water and carbonic acid being produced, whilst formiate of lead remains in the solution:—

$$\overbrace{2\,HO, C_8H_4O_{10}}^{\text{Tartaric Acid.}} + 6\,PbO_2 = 2\,\overbrace{(PbO, C_2HO_3)}^{\text{Formiate of Lead.}} + 4\,\overbrace{(PbO, CO_2)}^{\text{Carbonate of Lead.}} + 4\,HO.$$

The salts of silver, of gold, and of platinum are also reduced when boiled with tartaric acid.

Tartaric acid is extensively used by the calico printer and dyer for the removal of certain mordants from particular portions of the cloth. It is also used in the preparation of effervescing draughts with the bicarbonates of the alkalies.

(1107) *Tartrates.*—The tartaric is a dibasic acid, and it consequently has a strong tendency to form double salts, three varieties of which may be distinguished:—

1. Salts which contain protoxides only; such as—

Rochelle Salt, . .	$KO, NaO, C_8H_4O_{10}, 8\,Aq$
Cream of Tartar, . .	$KO, HO, C_8H_4O_{10}$
Tartrate of Copper and Potash,	$KO, CuO, C_8H_4O_{10}$

2. Salts which contain both protoxides and sesquioxides, but in which the sesquioxide is combined with the same proportion of acid as the protoxide; such as—

Tartrate of potash and iron . . .	$KO, Fe_2O_3, C_8H_4O_{10}$
Tartrate of potash and chrome . .	$KO, Cr_2O_3, C_8H_4O_{10} + 7\,Aq$
Tartrate of potash and uranium . .	$KO, U_2O_3, C_8H_4O_{10} + 2\,Aq$

3. Salts analogous to tartar emetic.

Tartar emetic, or tartrate of potash and antimony	$KO, SbO_3, C_8H_4O_{10} + Aq$
Tartrate of silver and antimony . .	$AgO, SbO_3, C_8H_4O_{10}$
Neutral tartrate of antimony . . .	$2\,(SbO_3), C_8H_4O_{10} + 2\,Aq$
Tartrate of potash and boracic acid .	$KO, BO_3, C_8H_4O_{10}$
Tartrate of potash and arsenious acid	$KO, AsO_3, C_8H_4O_{10} + 5\,Aq.$

The salts of this third class, with the exception of the compound with arsenious acid, are remarkable for the property which they possess when apparently anhydrous, of losing two additional equivalents of water, so as to present a composition which may be regarded as presenting a certain resemblance to that of tartaric anhydride (Gerhardt): $Sb O_2$ (or its equivalent representative BO_2), being able to occupy the position of 1 equivalent of hydrogen in the compound; thus:—

At ordinary temperatures,

Tartaric acid	consists of	$C_8H_6O_{12}$
Neutral tartrate of antimony	,,	$C_8H_4\ 2\,(SbO_2)O_{12}\ 2Aq$
Tartar emetic	,,	$C_8H_4K\ (SbO_2)O_{12}\ Aq$
Tartrate of silver and antimony	,,	$C_8H_4Ag(SbO_2)O_{12}$
Tartrate of potash and boracic acid	,,	$C_8H_4K\ (BO_2)\ O_{12}$

But when heated they become, respectively;

Tartaric anhydride	$C_8H_4O_{10}$
Neutral tartrate of antimony at 374°	$C_8H_2\ 2\,(SbO_2)\ O_{10}$
Tartar emetic dried at 392°	$C_8H_2K\ (SbO_2)\ O_{10}$
Tartrate of silver and antimony at 320°	$C_8H_2Ag\ (SbO_2)\ O_{10}$
Tartrate of potash and boracic acid at 506°	$C_8H_2K\ (BO_2)\ O_{10}$

Tartrate of Potash ($2\ KO, C_8H_4O_{10}$) crystallizes readily; it is somewhat deliquescent, and very soluble. The *bitartrate of potash* ($KO, HO, C_8H_4O_{10}$) is the ordinary source of the compounds of tartaric acid: it constitutes the crude tartar or *argol* of commerce, and is gradually deposited from all wines, forming a crust upon the inside of casks in which the wine is stored. This salt is very sparingly soluble in cold water, of which it requires about 180 parts for solution; boiling water dissolves about one-sixth of its weight of it, and deposits the salt in oblique rhombic prisms, which when pure are of snowy whiteness, forming common *cream of tartar*. It produces a gritty sensation under the teeth, and has a sour taste. When heated to redness in covered vessels the acid is decomposed, and a charred mass remains, consisting of carbonate of potash and unconsumed carbon; this product is often used in the laboratory under the name of *black flux*. If the salt be calcined with twice its weight of nitre, *white flux* is obtained; in this operation the carbon of the organic acid is completely burned, and carbonate of potash is left.

Tartrate of Potash and Soda, ($KO, NaO, C_8H_4O_{10}$, 8 Aq.)—The equivalent of basic water may be displaced from cream of tartar by soda, and then a double salt, often called *Rochelle salt*, is produced: it forms large beautiful crystals which have the appearance of six-sided prisms, one half of which only is developed. The tartrates of *lime*, *baryta*, and *magnesia* are sparingly soluble. *Iron* forms with potash and ammonia double tartrates which are used in medicine.

the potash salt when dried at 212° is anhydrous: the ammoniacal salt has the formula ($H_4NO, Fe_2O_3, C_8H_4O_{10} + 4$ or 5 Aq).

Borotartrate of Potash; Soluble Tartar ($KO, BO_3, C_8H_4O_{10}$; at 212°).—When 1 part of boracic acid, 2 parts of cream of tartar, and 24 of water are heated together, a solution is formed which on evaporation to dryness and treatment with alcohol (in order to remove the excess of boracic acid) furnishes the foregoing compound, in the form of a white non-crystalline powder, which is insoluble in alcohol, but very soluble in water; it becomes anhydrous at 212°, and if heated to 560° it loses 2 more equivalents of water, like tartar emetic under similar circumstances. This salt has been employed medicinally as a purgative.

Tartrates of Antimony.—Several tartrates of antimony may be formed. These salts are remarkable for the property which they possess, when apparently anhydrous, of losing 2 equivalents of water so as to present a composition corresponding to that of tartaric anhydride. The most important of these compounds is known as *tartarized antimony* or *tartar emetic* ($KO, SbO_3, C_8H_4O_{10}$, Aq), which has long been extensively used in medicine. Tartar emetic may be prepared in various ways; one of the best is the following:—3 parts of oxide of antimony (obtained by boiling to dryness sulphuric acid upon metallic antimony in an iron ladle) are mingled with 4 parts of cream of tartar, and made into a thin paste with water. This mixture is allowed to digest for some hours, and is then boiled with 6 or 8 parts of water. The solution thus formed is filtered while hot, and allowed to crystallize: as the liquid cools the salt is deposited in the form of square prisms, the primary form of which is an octohedron, with a rhombic base. Tartar emetic is soluble in about 15 parts of cold water; its solution slightly reddens litmus. This salt is slightly efflorescent; when dried at 212° it becomes anhydrous, and when heated to 400° it loses 2 additional equivalents of water, and then has a composition of $KO, SbO_3, C_8H_2O_8$; if this body be re-dissolved in water, it furnishes ordinary tartar emetic. A solution of tartarized antimony acts as a violent emetic and cathartic poison. Sulphuretted hydrogen throws down hydrated sulphide of antimony from it, and the alkalies and their carbonates occasion a precipitate of oxide of antimony.

The place of the potash in ordinary tartar emetic may be supplied by soda, ammonia, oxide of silver, and oxide of lead; the lead and silver salts thus formed lose 2 equivalents of water at a high temperature in the same manner as the potash salt.

A compound similar to tartar emetic may be formed with arsenious acid ($KO, AsO_3, C_8H_4O_{10}$).

The mother liquors from which tartar emetic has been prepared, often deposit a compound which may be crystallized with difficulty, in oblique rhombic prisms [$KO, SbO_3, 2\ HO, 2\ (C_8H_4O_{10})\ 5\ Aq.$; Knapp]: it is a combination of tartar emetic with an additional equivalent of tartaric acid. Knapp has also obtained a compound of tartar emetic with cream of tartar, [$KO, SbO_3, C_8H_4O_{10} + 3(KO, HO, C_8H_4O_{10})$] by boiling 5 parts of tartar emetic with 8 of cream of tartar, and a small quantity of water: it is deposited in sparingly soluble pearly scales. If oxide of antimony be dissolved in tartaric acid, the addition of alcohol in excess occasions the separation of a granular white precipitate, which, according to Berzelius, has a composition represented by the formula $2\ SbO_3, C_8H_4O_{10}, 2\ Aq.$ According to Péligot an acid tartrate [$3\ HO, SbO_3, 2\ (C_8H_4O_{10})\ 5\ Aq$] may be obtained in large crystals from a solution of oxide of antimony in excess of tartaric acid.

The presence of tartaric acid in solution is detected, if the liquid be moderately concentrated, by the addition of chloride of potassium; a few drops of free hydrochloric acid must also be added if the solution be neutral; under these circumstances a sparingly soluble bitartrate of potash falls, the quantity of which is much increased by briskly stirring the mixture. With salts of silver a sparingly soluble tartrate of silver is formed. This precipitate when placed on platinum foil swells up on the application of heat, and leaves a residue of pure silver. A solution of sulphate of lime is not precipitated by solutions of the tartrates.

The presence of tartaric acid in a solution which contains salts of iron or of copper prevents the precipitation of the oxides of these metals on the addition of an alkali. This property is sometimes taken advantage of in the operations of analysis.

The tartrates when heated strongly become blackened and are decomposed, emitting an odour of burnt sugar.

(1108) *Action of heat on Tartaric Acid.*—The action of heat upon tartaric acid is remarkable. If heated to about 340° it fuses, and without losing weight is changed into two metameric acids, *metatartaric* and *isotartaric* acids. Metatartaric acid forms a deliquescent uncrystallizable mass: it is dibasic, but its salts are more soluble than the ordinary tartrates, into which they are transformed by boiling their solutions.

Isotartaric acid ($HO, C_8H_5O_{11}$) assumes the form of a vitreous deliquescent mass. It is a monobasic acid, and forms salts, which are isomeric with the bitartrates, but are much more soluble; by boiling their solutions they become converted into ordinary bitartrates.

tartaric acid be heated to 374°, it fuses; two equiva- acid lose one equivalent of water, and thus become into a new acid, termed by Fremy the *tartralic.* In this compound, the mass is dissolved in water neutralized with carbonate of baryta; a soluble tartralate of is formed, while any undecomposed tartaric acid remains in the form of an insoluble tartrate of baryta. Aqueous of tartralic acid and of its salts, if boiled, pass quickly the ordinary tartrates, and the same change takes place more at ordinary temperatures. If tartaric acid be kept longer in half its basic water is expelled, and *tartrelic acid* is formed, gives a syrupy precipitate with salts of baryta. The acids last described are probably mere combinations of the ydrous with the crystallized tartaric acid in different pro- tions. If the temperature of the fused tartaric acid be nously maintained for some time at 374°, all its basic water is en off, and anhydrous tartaric acid remains in the form of a te porous mass; in order to remove any unchanged tartaric d, it may be washed first with cold water, and then with alcohol, r which it should be dried *in vacuo.* It is insoluble in water, ohol, and ether, but if allowed to remain long moist it gradually omes soluble, and is converted into crystallized tartaric acid. e last three acids present a relation somewhat analogous to those the varieties of phosphoric acid; for instance, if they be compared h 2 equivalents of tartaric acid, the relations will be thus resented :—

Anhydrous tartaric acid . .	$C_{16}H_8O_{20}$
Tartrelic acid	$2\ HO, C_{16}H_8O_{20}$
Tartralic acid	$3\ HO, C_{16}H_8O_{20}$
Crystallized tartaric acid . .	$4\ HO, C_{16}H_8O_{20}$

By heating crystallized tartaric acid to about 400° in a retort, acid liquor distils, which contains acetic acid, and a new acid med *pyruvic* or *pyroracemic* acid ($2\ HO, C_{12}H_6O_{10}$). It forms insoluble salt with lead, and a sparingly soluble one with silver.

Pyruvic acid is characterized by the production of a red solution en mixed with a solution of a protosalt of iron. If its salts be pared in the cold, they are crystallizable; but if the acid be urated with bases at a high temperature, the salts are gummy and not crystallize. During the distillation of tartaric acid, a quantity a second new acid is also formed; it crystallizes in oblique mbic prisms, and has received the name of *pyrotartaric acid* HO, $C_{10}H_6O_6$); it contains two equivalents of carbonic acid less than the pyruvic. Pyrotartaric acid is dibasic, it forms both neutral and acid salts; the latter crystallize with facility.

(1109) *Racemic,* or *Paratartaric Acid* ($2\ HO, C_8H_4O_{10}+2\ Aq$). Some varieties of the grape, particularly those grown in the Vosges district, present a singular modification of tartaric acid, which is metameric with the tartaric acid, and equal amounts of the two acids saturate equal quantities of the same base. This acid, as has been already stated (1105), is plainly a compound of dextro-tartaric and lævo-tartaric acids; it is without action upon polarized light.

Racemic acid generally accompanies tartaric acid in greater or less quantity. It is obtained from the racemate of lime by a process precisely similar to that used for procuring tartaric acid from the tartrate of lime. Racemic acid crystallizes more readily than the tartaric in efflorescent, oblique rhombic prisms, which contain two equivalents of water of crystallization; this water is expelled by a temperature of 212°. Racemic acid is less soluble in alcohol than tartaric acid, and precipitates solutions of sulphate and nitrate of lime as well as those of chloride of calcium; the racemate of lime is soluble in hydrochloric acid, and is precipitated unchanged on adding ammonia. These reactions distinguish it easily from tartaric acid. When heated, racemic acid loses water and forms acids corresponding with the tartralic and tartrelic; it may ultimately be rendered anhydrous: the products of its distillation are the same as those of tartaric acid. With antimony it forms a salt which corresponds to tartar emetic, but it crystallizes in radiated tufts of needles, not in octohedra. The ordinary salts of racemic acid occur in symmetrical crystals, and with the exception of the double racemate of soda and ammonia and of the racemate of cinchonicine and quinicine, they are not hemihedral.

(1110) *Conversion of Tartaric into Racemic Acid.*—Pasteur has succeeded in converting both the varieties of tartaric, into racemic acid: for this purpose either the dextro-tartrate or the lævo-tartrate of cinchonia is exposed to a gradually rising temperature; the salt first becomes converted into tartrate of cinchonicine; if the heat be continued, the cinchonicine loses water, it becomes coloured, and is transformed into quinoidine. At the same time the tartaric acid also becomes modified, and after it has been exposed to a temperature of 340° for five or six hours, a portion of it is changed into racemic acid. The black resinoid mass into which the salt has been converted, is treated with boiling water, and the liquid thus obtained is mixed with an excess of chloride of calcium by which the whole of the racemic acid is precipitated in the form of racemate of lime, from which the acid may readily be extracted. During the process of converting the tartrate of cinchonia into the racemate, another modification of tartaric acid is formed; it has been termed by Pasteur, *inactive tartaric acid*, in allusion to its want of action upon polarized light. It crystallizes beautifully, and forms crystallizable salts. This inactive acid is distinguished from racemic acid by the circumstance, that it does not admit of being resolved into dextrotartaric and lævotartaric acids.

The following are the modifications of tartaric acid which are at present known:—

1. Tartaric anhydride (insoluble) . .	$C_8H_4O_{10}$
2. Dextrotartaric acid	$2\ HO,\ C_8H_4O_{10}$
3. Lævotartaric acid	$2\ HO,\ C_8H_4O_{10}$
4. Racemic acid.	$2\ HO,\ C_8H_4O_{10}$
5. Inactive tartaric acid	$2\ HO,\ C_8H_4O_{10}$
6. Metatartaric acid	$2\ HO,\ C_8H_4O_{10}$
7. Isotartaric acid	$HO,\ C_8H_5O_{11}$
8. Tartralic acid	$HO,\ C_8H_4O_{10}$
9. Tartrelic acid	$1\tfrac{1}{2}HO,\ C_8H_4O_{10}$.

3. *Malic Acid, and its Derivatives.*

(1111) MALIC ACID ($2\ HO,\ C_8H_4O_8$).—This acid is extensively diffused through the vegetable kingdom; it occurs abundantly in most acidulous fruits, particularly in unripe apples, gooseberries, and currants, in which it is accompanied by citric acid. The footstalks of the garden rhubarb also contain it in considerable quantity, mixed with oxalic and phosphoric acids, and they furnish a convenient source of malic acid; but it is usually extracted from the unripe berries of the mountain ash. The dried leaves of the tobacco plant are also rich in bimalate of lime.

In order to obtain the acid, the expressed juice either of the mountain ash berries or of the leaf stalks of the rhubarb, is nearly neutralized with milk of lime, and a certain quantity of chloride of calcium is added in order to decompose the malate of potash which always accompanies the free acid. A precipitate is thus formed which contains the citric, phosphoric, and tartaric acids in combination with lime. The liquid must be left with a feeble acid reaction, in order to avoid the subsequent precipitation of the colouring matter. The clear solution is then to be filtered, and the filtrate boiled for several hours: neutral malate of lime is thus gradually separated in the form of an insoluble powder. After this precipitate has been washed with cold water, it is to be added in small portions at a time, so long as it continues to be dissolved, to hot dilute nitric acid (containing one part of acid to ten of water). The liquid thus obtained is to be filtered, and set aside to crystallize: well-defined crystals of bimalate of lime are then deposited. The bimalate thus obtained, may be purified by treating it with animal charcoal and recrystallizing it from water. Its solution may afterwards be converted into malate of lead by the addition of acetate of lead, and the malate of lead when decomposed with sulphuric acid, yields free malic acid, from which the last traces of lead may be removed by means of sulphuretted hydrogen.

Properties.—The aqueous solution of malic acid when evaporated to the consistence of syrup and left in a warm place, gradually deposits radiated masses composed of brilliant four or six-sided prisms. They are deliquescent in a moist air, and are soluble in alcohol; when heated they undergo fusion below 212°. Malic acid has a very sour taste; its solution unless quite pure becomes mouldy and viscid when kept.

Malic acid, when heated to 350° is decomposed, water is expelled, and two isomeric acids, the *malæic* and the *fumaric*, are formed, and at the same time malæic anhydride is obtained:—

$$\overbrace{2\,(2\,HO,\,C_8H_4O_8)}^{\text{Malæic Acid.}} = 4\,HO + \overbrace{2\,HO,\,C_8H_2O_6}^{\text{Fumaric Acid.}} + \overbrace{2\,HO,\,C_8H_2O_6}^{\text{Malæic Acid.}}.$$

Hydrated malæic acid when maintained in a state of fusion at 300°, is converted into a crystalline mass of fumaric acid. If distilled by a temperature suddenly elevated to 460°, malæic anhydride is formed. Sulphuric acid, when heated with malic acid, decomposes it and liberates carbonic oxide. Nitric acid converts it first into fumaric and then into oxalic acid.

When malic acid is fused with hydrate of potash at a temperature of 300°, hydrogen is disengaged, and oxalate and acetate of potash are formed:—

$$2\,\overbrace{HO,\,C_8H_4O_8}^{\text{Malic Acid.}} + 3\,(KO,HO) = \overbrace{2\,KO,\,C_4O_6}^{\substack{\text{Oxalate}\\ \text{of Potash.}}} + \overbrace{KO,\,C_4H_3O_3}^{\substack{\text{Acetate}\\ \text{of Potash.}}} + 4\,HO + H_2.$$

(1112) *Malates.*—The malic is a dibasic acid, and has a strong tendency to form acid salts. The bimalate of ammonia and the bimalate of lime are readily obtained in large regular crystals; but its most characteristic salt is the *malate of lead* ($2\,PbO,\,C_8H_4O_8,\,6\,Aq$), which when first precipitated is amorphous, but if left in the liquid, becomes converted into radiated tufts of silky needles. It is fusible into a pasty mass at a temperature below that of boiling water. Malic acid, like the tartaric, prevents the precipitation of iron from its solution by the alkalies. Malic acid gives no precipitate with lime water, either when cold or hot; but, by evaporation of the liquid, a crystallized malate of lime is produced, which is dissolved by boiling water. These characters distinguish the malic from oxalic, tartaric, racemic, and citric acids. Most of the malates are soluble in water, but not in alcohol. Many of the malates, such as those of lime and baryta, when heated to 400°, lose two equivalents of water, and become converted into fumarates, from which fumaric acid may be obtained in characteristic broad, slender, sparingly soluble, striated prisms.

Bimalate of Ammonia ($H_4NO, HO, C_8H_4O_8$) is readily obtained by dividing a solution of malic acid into two equal portions, exactly neutralizing one with ammonia, and then adding to it the other portion of the acid; on evaporation, brilliant right rhombic prisms are formed. Bimalate of ammonia, when submitted to distillation, is converted into a brick-coloured powder, termed *fumarimide*:—

$$\overbrace{H_4NO,\ HO,\ C_8H_4O_8}^{\text{Bimalate of Ammonia,}} = \overbrace{C_8H_3NO_4}^{\text{Fumarimide.}} + 6\ HO.$$

Bimalate of Lime ($CaO, HO, C_8H_4O_8$, 8 Aq).—This salt is obtained in beautiful transparent rhombic prisms, by dissolving the neutral malate of lime in hot dilute nitric acid, and allowing the solution to cool. It is sparingly soluble in cold water.

The *neutral malate of lime* exists in two modifications: one of these ($2\ CaO, C_8H_4O_8$, 4 Aq) is readily soluble. It is obtained by neutralizing malic acid or the bimalate of lime with milk of lime; the solution may be evaporated at ordinary temperatures, and deposits large brilliant crystalline plates. If the solution of this salt be boiled for some hours, it gradually deposits a sparingly soluble, granular, crystalline powder, which when analysed is found to contain only two equivalents of water of crystallization, but has in other respects the same composition as the soluble malate. The soluble form of malate of lime may also be obtained with five and with six equivalents of water. If malate of lime be placed beneath a layer of water, in a vessel loosely covered, it gradually undergoes decomposition, carbonic acid is disengaged, and a mixture of lactic, acetic, and succinic (1181) acids is formed. This change is accelerated by the addition of a small quantity of yeast to the mixture:—

$$\overbrace{3\ (2\ HO,\ C_8H_4O_8)}^{\text{Malic Acid.}} = \overbrace{2\ (2\ HO,\ C_8H_4O_6)}^{\text{Succinic Acid.}} + \overbrace{HO,\ C_4H_3O_3}^{\text{Acetic Acid.}} + 4\ CO_2 + 2\ HO.$$

Malate of zinc ($2ZnO, C_8H_4O_8$, 6 Aq) is sparingly soluble in cold water, but is taken up by ten times its weight of boiling water; short, rectangular, brilliant, very hard prisms are deposited as it cools. A bimalate of zinc (ZnO, HO, $C_8H_4O_8$, 4 Aq) may also be obtained in octohedral crystals.

Besides the neutral malate of lead, a *basic malate* (4 PbO, $C_8H_4O_8$) may be obtained by precipitating a soluble malate by subacetate of lead; it is not fusible in boiling water.

Malate of silver forms a white, anhydrous, insoluble powder.

(1113) *Metameric Modifications of Malic Acid.*—Malic acid has been ascertained by Pasteur to exist in two modifications, which may be distinguished by the letters a and β; the variety a, which exerts a left-handed rotatory action upon a ray of polarized light, is the ordinary form of the acid; some of its salts exert a rotation to the left, others to the right. The variety β is destitute of any such rotatory power, and hence is termed *inactive malic acid.* The latter modification of the acid presents scarcely any perceptible chemical difference from the acid a, but it crystallizes rather more readily from its aqueous solution, since it is somewhat less soluble and is not deliquescent: it also requires a temperature of 272° for its fusion: when heated a few degrees beyond this point it is decomposed, and furnishes the same compounds as the ordinary form of the acid. Inactive malic acid is procured by the action of nitrous acid upon inactive aspartic acid (1115); during this reaction nitrogen escapes in abundance, and if the acid liquid be supersaturated with ammonia when the disengagement of gas has ceased, the addition of a solution of acetate of lead causes the separation of a precipitate of inactive malate of lead; from this malate of lead sulphuretted hydrogen liberates the inactive acid, β.

It will be observed that the formula of malic acid differs from that of the tartaric, by containing two equivalents less of oxygen.

(1114) *Amides of Malic Acid—Asparagin.*—Malic acid, like the dibasic acids in general, forms two amides; one of these possesses the properties of an acid, and has been termed *malamic acid* (HO, H_2N, $C_8H_4O_7$), which is isomeric with aspartic acid, if not identical with it.

Asparagin ($C_8H_8N_2O_6$, 2 Aq).—This crystalline body is isomeric with malamide. It is extracted from the young shoots of the asparagus and of the climbing vetch, from the roots of the marsh mallow, and from several other plants. It may generally be procured in crystals by simply evaporating the expressed juice of one of these plants. The brown crystals thus obtained may be purified by treatment with animal charcoal and re-crystallization. Asparagin, when pure, forms beautiful octohedra, or rhombic prisms, which are soluble in about 60 parts of cold water, and are freely dissolved by boiling water, by dilute acids and alkalies, and by proof spirit. It has a mawkish and cooling taste. When dissolved in water, or in alkaline solutions, it exerts a left-handed rotation upon a ray of polarized light; but if dissolved in acids it produces a right-handed rotation of the ray. Asparagin is chiefly remarkable for the facility with which it is decomposed into aspartic acid and ammonia, when its aqueous solution is heated with alkalies or with acids:—

$$\overbrace{C_8H_8N_2O_6, 2\,HO}^{\text{Asparagin.}} = \overbrace{HO, C_8H_6NO_7}^{\text{Aspartic Acid.}} + H_3N\,.$$

When an aqueous solution of asparagin is heated under pressure, it is wholly converted into aspartate of ammonia; and the same effect takes place slowly when the solution is exposed to a temperature of 212° for a few days. By a moderate heat, asparagin loses its 2 equivalents of water of crystallization, and in its anhydrous form is isomeric with malamide.

Piria found that if the expressed juice of the vetch were allowed to putrefy, the asparagin which it contained was gradually converted into succinate of ammonia, by the assimilation of 2 equivalents of hydrogen:—

$$\overbrace{C_8H_8N_2O_6, 2\,HO}^{\text{Asparagin.}} + H_2 = 2\,\overbrace{H_4NO, C_8H_4O_6}^{\text{Succinate of Ammonia.}}\,.$$

When asparagin is treated with nitric acid which has been saturated with nitrous acid, it is converted into malic acid, whilst nitrogen is disengaged:—

$$\overbrace{C_8H_8N_2O_6, 2\,HO}^{\text{Asparagin.}} + 2\,NO_3 = \overbrace{2\,HO, C_8H_4O_8}^{\text{Malic Acid.}} + 4\,N + 4\,HO\,.$$

This reaction is similar to that which occurs when the amides are thus treated, and hence Piria was led to regard asparagin as identical with malamide; but on decomposing malic ether by means of ammonia, a substance is obtained which is isomeric with asparagin, but not identical with it. Asparagin forms combinations with several of the acids in definite proportions; thus, the nitrate, the oxalate, the tartrate, and the hydrochlorate of asparagin may be obtained in crystals without difficulty. It also combines with bases, and even displaces acetic acid from acetate of lead.

(1115) *Aspartic Acid* ($HO, C_8H_6NO_7$).—If aspartate of ammonia be boiled with baryta till the ammonia is entirely expelled, aspartate of baryta is formed; and from this salt the baryta may be precipitated by the cautious addition of sulphuric acid: on evaporating the solution thus obtained, aspartic acid crystallizes in thin rectangular tables which have a silky lustre. It is soluble both in acids and alkalies; when dissolved in the alkalies it produces left-handed rotation of the plane of polarization, but if dissolved in acids the rotation is to the right.

Pasteur has discovered the existence of a second modification of aspartic acid which is without action upon polarized light. This *inactive* acid is obtained by heating bimalate of ammonia to about 360°, and boiling the residue (fumarimide, $C_8H_3NO_4$) for some hours with hydrochloric acid. The solution, when evaporated, yields crystals of hydrochlorate of aspartic acid ($HO, C_8H_6NO_7, HCl$). These crystals must be dissolved in water, and the solution divided into two equal portions; one of these is to be exactly neutralized by the addition of ammonia, and then added to the second portion; as the liquid cools, crystals of inactive aspartic acid are deposited in abundance. It is somewhat more soluble than the active variety, but in other respects resembles it in chemical properties.

Most of the aspartates are readily soluble in water. The acid appears in a few cases to form subsalts. Aspartic acid, when dissolved in nitric acid and saturated with nitrous acid, yields malic acid, whilst nitrogen is disengaged; and if the inactive variety be employed, the malic acid which is obtained is likewise of the inactive form (1113):—

$$\overbrace{HO, C_8H_6NO_7}^{\text{Aspartic Acid.}} + NO_3 = 2\,\overbrace{HO, C_8H_4O_8}^{\text{Malic Acid.}} + 2\,N + HO\,.$$

4. *Citric Acid, and its Derivatives.*

(1116) CITRIC ACID ($3\,HO, C_{12}H_5O_{11}, 2\,Aq$; Liebig) is a powerful tribasic vegetable acid, found principally in the fruits of the *aurantiaceæ*. Citric acid is also of frequent occurrence in other acidulous fruits, such as gooseberries, raspberries, strawberries, cherries, and tamarinds. It is extracted by neutralizing the juice of the lime or of the lemon with chalk, and decomposing the insoluble citrate of lime with sulphuric acid, by a process similar to that directed for the preparation of tartaric acid. Citric acid is very soluble in water; the solution has an agreeable acid taste: it is likewise soluble in alcohol, but not in ether. If the cold saturated aqueous solution be allowed to evaporate spontaneously, it crystallizes in colourless, transparent, rhombic prisms, which constitute the commercial citric acid. When heated to 212° these crystals melt, and lose 2 equivalents of water; the remaining compound consists of $C_{12}H_8O_{14}$, which Liebig regards as a tri-

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siderable: these phenomena depend upon the circumstance, that the citrate of lime is less soluble in boiling than in cold water. Crude citrate of lime, obtained by saturating lemon-juice with chalk, cannot be preserved in a moist state without undergoing decomposition: it ferments, disengages a mixture of hydrogen and carbonic acid gases, and a mixture of acetate and of butyrate of lime is formed. This change is accelerated by the addition of a small quantity of yeast to the mixture.

The citrates of the alkalies are all soluble in water; so also are many of the citrates of the heavier metals; the citrates of the earths with 3 equivalents of the earthy base are insoluble; but they become dissolved by adding an excess of citric acid, and thus forming salts, which contain 1 equivalent or 2 equivalents of basic water. The *acid citrate of lime* consists of $2\ CaO,\ HO,\ C_{12}H_5O_{11},\ 2\ Aq$, and forms brilliant foliated crystals.

The citrates of the neutral type, when heated, present a remarkable peculiarity, which led Berzelius to propose the formula $(HO,\ C_4H_2O_4)$, or rather $(3\ HO,\ C_{12}H_6O_{12})$, as the true representative of citric acid. Assuming, for example, that the formula for citrate of potash is $(3\ KO,\ C_{12}H_6O_{12},\ Aq)$, this salt, by a heat of 212°, loses 2 equivalents of water, and is converted into $(3\ KO,\ C_{12}H_5O_{11})$, which is Liebig's formula for anhydrous citrate of potash. This residue appears not to be a simple citrate of potash, though on redissolving it in water the original citrate is reproduced; but it presents the characters of a mixture of citrate and aconitate of potash; for if the salt be treated with absolute alcohol, and decomposed by dry hydrochloric acid, so as to exclude the access of water, chloride of potassium is formed, and the citric acid which is set free is found to be mixed with aconitic acid, which may be separated from the citric acid without difficulty. The same phenomenon is exhibited by citrate of silver: if this salt be precipitated at a temperature below 50° F. it has a composition represented by the formula $(3\ AgO,\ C_{12}H_6O_{12})$, but at all higher temperatures it contains an equivalent less of water, $(3\ AgO,\ C_{12}H_5O_{11})$. Now, if this latter salt be treated like the potash salt, with dry hydrochloric acid in absolute alcohol, 3 equivalents of the compound yield by decomposition 9 equivalents of chloride of silver, 2 equivalents of hydrated citric, and 1 equivalent of hydrated aconitic acid:—

$$3\overbrace{(3\ AgO,\ C_{12}H_5O_{11})}^{\text{Citrate of Silver.}} + 9\ HCl = 9\ AgCl + \overbrace{(3\ HO,\ C_{12}H_3O_9)}^{\text{Aconitic Acid.}} + \overbrace{2(3\ HO,\ C_{12}H_6O_{12})}^{\text{Citric Acid.}}.$$

When citrate of silver is heated to 212° in a current of hydrogen gas, it becomes partially reduced, and a brown powder is formed, which, according to Wöhler, is a citrate of suboxide of silver. Water extracts citric acid from it, and dissolves it in small proportion, producing a red solution. This solution, when boiled, deposits reduced silver.

Citrate of peroxide of iron is prepared by dissolving hydrated peroxide of iron in a hot solution of citric acid. It has a sweetish taste, and forms a deep brown liquid, from which it is precipitated by the addition of alcohol. When its solution is evaporated in shallow vessels, it forms brilliant scales of a resinous aspect; and in this form it is used in medicine.

Tricitrate of Lead (dried at 250°; $3\ PbO,\ C_{12}H_5O_{11}$).—This salt is prepared by precipitating a hot alcoholic solution of tribasic citrate of soda by an alcoholic solution of acetate of lead; it forms a granular sparingly soluble powder. If this salt be digested with ammonia, it forms a heavy crystalline powder ($4\ PbO,\ C_{12}H_5O_{11},\ HO$); and if the tricitrate be digested with basic acetate of lead, a salt with a still larger proportion of base ($6\ PbO,\ C_{12}H_5O_{11},\ HO$) is formed.

Tricitrate of copper is soluble; a green crystalline, sparingly soluble, *subcitrate* ($4\ CuO,\ C_{12}H_5O_{11},\ 3\ HO$) is formed by boiling a solution of acetate of copper with citric acid.

A *tribasic citric ether* ($3\ C_4H_5O,\ C_{12}H_5O_{11}$) may be obtained by saturating an alcoholic solution of citric acid with hydrochloric acid, neutralizing with carbonate of soda, and agitating the liquid with ordinary ether. The ethereal solution rises to the surface on standing; and if the ethylic ether be expelled by the heat of a water-bath, citric ether is left as a colourless oily liquid.

(1117) *Action of Heat upon Citric Acid.*—If citric acid be exposed to a high temperature, it undergoes decomposition: at a temperature of between 300° and 350°, water, acetone, and a mixture of carbonic acid and carbonic oxide gases are disengaged, and a brownish residue is obtained, which is in great part soluble in ether; this residue consists of a peculiar acid, the *aconitic*, ($3\ HO,\ C_{12}H_3O_9$), which exists also in the different varieties of monkshood (*aconitum*) and marestail (*equisetum*). Aconitic acid is isomeric with fumaric and malæic acids. Hydrated aconitic acid contains the elements of 2 equivalents of water less than hydrated citric acid; $3\ HO,\ C_{12}H_3O_9 + 2\ HO = 3\ HO,\ C_{12}H_5O_{11}$. Indeed, aconitic acid derives its principal interest from its close connexion with citric acid, and from the light which its composition throws upon some apparent anomalies in relation to the separation of water from the crystallized acid and its salts (1116 *bis*). The aconitates the alkalies give no immediate precipitate in solutions of the ts of baryta, lime, magnesia, and zinc, but they produce white cipitates in solutions of lead and of silver.

If citric acid be heated beyond the point at which aconitic acid formed, the aconitic acid is itself decomposed, carbonic acid capes, and the principal product consists of a volatile, oily-look-g acid liquid, which contains a mixture of two isomeric acids, ne of which, the *itaconic*, crystallizes with facility, and the other, ermed *citraconic, pyrocitric* or *citribic acid*, is much more soluble; oth have the formula ($2\,HO, C_{10}H_4O_6$). 1 equivalent of hydrated conitic acid contains the elements of 1 equivalent of hydrated taconic or citraconic acid, and 2 equivalents of carbonic acid;

$$\overbrace{3\,HO, C_{12}H_3O_9}^{\text{Aconitic Acid.}} = \overbrace{2\,HO, C_{10}H_4O_6}^{\text{Itaconic Acid.}} + 2\,CO_2.$$

A considerable quantity of citraconic anhydride passes over with the hydrated acids during the distillation. Citraconic acid is also obtained during the distillation of lactic acid. When citraconic is treated with nitric acid it is partially decomposed, and converted into oxalic acid, whilst a nitro-acid, probably ($2\,HO, C_{10}H_3, NO_4, O_6$) is produced, and at the same time a new acid, isomeric with the citraconic, is formed, termed *mesaconic acid.* The latter may be obtained in minute crystals, which are sparingly soluble in water.

5. *Meconic Acid, and its Derivatives.*

(1118) Meconic Acid ($3\,HO, C_{14}HO_{11}, 6\,Aq$). This acid (which derives its name from *μήκων*, a poppy) is contained in the milky juice of the *papaveraceæ*. It is extracted from a concentrated aqueous infusion of opium by nearly neutralizing it with milk of lime and adding a solution of chloride of calcium; the meconate of lime being nearly insoluble, is thus precipitated. In order to isolate the acid, one part of meconate of lime is mixed with 10 parts of water at 190°, and decomposed by the addition of hydrochloric acid in considerable excess; the meconic acid crystallizes from the solution in scales, which, however, are considerably coloured. They must be digested with purified animal charcoal, and re-crystallized, but they cannot be obtained colourless without considerable difficulty. Meconic acid is sparingly soluble in cold water, but is readily dissolved by it when hot; it is also soluble in alcohol and in ether. Its solutions have an acid, astringent taste. When its crystals are heated to 212°, 6 equivalents of water are expelled. The aqueous solution of meconic acid is decomposed by ebullition, and carbonic acid gradually escapes.

This change is effected more rapidly if some mineral acid, such as the sulphuric or hydrochloric, be added to the liquid. Similar results are obtained if the crystallized acid be heated to 250°. In all these cases, a new acid, the comenic, is obtained :—

$$3\,\overbrace{HO, C_{14}HO_{11}}^{\text{Meconic Acid.}} = 2\,\overbrace{HO, C_{12}H_2O_8}^{\text{Comenic Acid.}} + 2\,CO_2.$$

Meconates.—Meconic acid is tribasic, the formula of its neutral salts being $3\,MO, C_{14}HO_{11}$. The meconates of the alkalies are soluble. The neutral meconates of lime, baryta, lead, copper, and silver are nearly insoluble in water, but are soluble in acetic acid. Meconate of silver when heated is decomposed with explosion.

It is sometimes important for medico-legal purposes to be able to ascertain the presence of meconic acid in cases where opium is suspected to have been administered as a poison. With this view the following process may be adopted :—The solution is to be mixed with acetate of lead, an impure meconate of lead is thus precipitated if meconic acid be present; the precipitate after it has been washed is decomposed by sulphuretted hydrogen, and the meconic acid thus set at liberty is concentrated by evaporation at a temperature not exceeding 160°; a very dilute solution of perchloride of iron is then added to the concentrated liquid. If meconic acid be present it strikes a deep blood-red colour, which may be distinguished from that due to sulphocyanide of potassium by the effect of the addition of a few drops of sulphuric acid with a fragment of zinc; if the colour be due to the sulphocyanide, the red tint will disappear, and sulphuretted hydrogen will be extricated; but if the compound contain meconic acid, the colour will not be affected: a solution of terchloride of gold also discharges the colour of the sulphocyanide of iron, but is without effect upon the meconate.

(1119) *Comenic Acid* ($2\,HO, C_{12}H_2O_8$) is dibasic. It is sparingly soluble in water, and crystallizes in hard warty nodules. Nitric acid rapidly decomposes it into oxalic, carbonic, and hydrocyanic acids. This acid, like the preceding one, gives a blood-red solution with the persalts of iron, and a white precipitate with acetate of lead, but it gives no precipitate with salts of baryta.

If either the meconic or the comenic acid be distilled, a new monobasic acid, pyromeconic acid ($HO, C_{10}H_3O_5$), is sublimed :—

$$\overbrace{2\,HO, C_{12}H_2O_8}^{\text{Comenic Acid.}} = \overbrace{HO, C_{10}H_3O_5}^{\text{Pyromeconic Acid.}} + 2\,CO_2.$$

This acid is isomeric with the pyromucic, but is distinguished from it by yielding with the persalts of iron, a solution of a blood-red colour, and by giving no precipitate with a solution of subacetate of lead.

6. *Different Varieties of Tannic Acid.*

(1120) The term *tannin* was formerly applied to the various forms of the astringent principle which were employed in the process of tanning hides. Most of these substances are now known to possess an acid reaction; but it has been ascertained that there are several distinct compounds which resemble each other in properties, though they possess a different chemical composition. These astringent principles are very extensively diffused throughout the vegetable kingdom. The bark and leaves of most forest trees, such as the oak, the elm, the willow, the horse-chesnut, and the pine,—and many fruit trees, such as the pear and plum, contain tannin in notable quantity. The wood and bark of many shrubs, such as the sumach and the whortleberry,—and the roots of the tormentilla, and bistort, are also powerfully astringent, owing to the presence of one of the forms of tannin. Coffee and tea, as well as Paraguay tea, likewise contain a modification of this astringent principle. All these bodies, except coffee, precipitate the persalts of iron of a bluish-black colour, or if a free acid be present, the solution assumes a dark-green colour. Many vegetables contain an astringent principle which precipitates the salts of iron of a dark-green instead of a blue colour: catechu and kino offer good instances of this variety of tannin. Some few astringent plants yield an infusion which precipitates iron of a grey colour, among which are matricaria, rhatany (*krameria triandra*), and the common nettle (*urtica urens*). Tannic acid in all its forms rapidly absorbs oxygen when moist.

The most important of these acids, and the one which has been most accurately studied, is the tannic acid of the gall nut, or *gallotannic* acid: that of the oak or *quercitannic* acid is also a distinct species (Stenhouse), as well as that of the fustic (*morus tinctoria*): *moritannic acid*, as the latter variety is termed, is a yellow crystalline solid, which, according to the experiments of Wagner, may be represented by the formula ($C_{36}H_{16}O_{10}$). *Quinotannic* acid, or the tannin of the cinchona, according to Hlasiwetz, is represented by the formula ($C_{28}H_{19}O_{17}$); and there is no doubt that the *mimotannic* acid or tannin of the catechu is a distinct variety, although from its proneness to change, the true composition of this substance is uncertain. Kino, valonia (the acorn cups of the *quercus ægilops*), and divi-divi (the pod of the legume of *cæsalpinia coriaria*), all contain powerfully astringent compounds which, according to Stenhouse, are distinct from gallotannic acid.

(1121) GALLOTANNIC ACID; *tannic acid* ($C_{54}H_{22}O_{34}$; Strecker). —This acid is obtained in a state of purity from the gall nut, an excrescence produced upon the leaves of a species of oak (*quercus infectoria*), by the puncture of a small hymenopterous insect. The gall nut contains as much as two-thirds of its weight of tannic acid, and about two per cent. of gallic acid (Guibourt). In order to extract the tannic acid, Pelouze directs the gall nuts to be reduced to powder, and digested with about an equal weight of washed ether; the decanted liquid separates on standing, into two portions, the denser of which is of a yellow colour, and consists of a concentrated aqueous solution of tannic acid; the other portion is of a greenish colour, and is composed of ether holding gallic acid and colouring matter in solution. The yellow solution, when evaporated to dryness, yields a porous, pale buff-coloured residue of amorphous gallotannic acid. According to Stenhouse the tannic acid of sumach is identical with that of the gall nut, but it is not readily obtained in a pure form. Gallotannic acid is freely soluble in water; it reddens litmus paper, and dissolves the carbonates with effervescence. It has a purely and intensely astringent taste: it is soluble in dilute alcohol, but sparingly so in ether. Its diluted aqueous solution slowly absorbs oxygen from the air, and is converted into gallic acid; this process is favoured by the presence of a particular ferment which is contained in the gall nut. A solution of tannic acid in water is coagulated by chloride of potassium, and by many other salts. Sulphuric, hydrochloric, phosphoric, and some other acids also diminish its solubility, and precipitate it from a concentrated aqueous solution. Nitric acid converts it into oxalic and saccharic acids. If boiled with dilute sulphuric, or with hydrochloric acid, it is converted into sugar and gallic acid (Strecker); the latter crystallizes on cooling, whilst the glucose remains in solution:—

$$\overbrace{C_{54}H_{22}O_{34}}^{\text{Gallotannic Acid.}} + 10\,HO = 3\,\overbrace{(3\,HO, C_{14}H_3O_7)}^{\text{Gallic Acid.}} + \overbrace{C_{12}H_{12}O_{12}, 2\,Aq.}^{\text{Glucose.}}$$

A boiling concentrated solution of potash also decomposes tannic acid and occasions the formation of gallic acid. If air be admitted to the mixture, the acid last named is in turn decomposed into a black ulmin-like substance.

Gallotannates.—The composition of these salts is but imperfectly known, and there is considerable uncertainty whether the acid should be regarded as dibasic or as tribasic. A solution of gallotannic acid occasions a violet black precipitate in solutions of the persalts of iron. It also causes precipitates in the solutions of the salts of morphia, quinia, brucia, and many other vegetable bases; these precipitates consist of gallotannates of the bases, and are readily soluble in acetic acid. The gallotannates of lead and of antimony are white and insoluble. Those of the alkalies are soluble; their solutions have an astringent taste, and do not precipitate gelatin until some acid is added to liberate the gallotannic acid from the base. If the solutions of these salts be exposed to the air, especially if the base be in excess, they rapidly become brown, and are decomposed with absorption of oxygen. None of the gallotannates can be obtained in crystals.

The basis of ordinary writing ink is gallotannate of iron. Various recipes are given for its preparation: the following furnishes a very good ink:—Digest three quarters of a pound of bruised nut galls in a gallon of cold water, then add six ounces of sulphate of iron with an equal weight of gum arabic, and four or five drops of kreasote to prevent the ink from becoming mouldy. Let this mixture digest at ordinary temperatures for two or three weeks with occasional agitation; then allow it settle, and decant for use. Oxalic acid and chlorine water readily discharge the colour of writing ink, and they may be employed to remove ink-stains from linen. An ink-spot when washed with an alkaline soap becomes yellow, forming what is familiarly known as an iron-mould. This yellow stain is due to the oxide of iron, which constitutes the basis of the ink, and which has attached itself to the cloth, whilst the alkali of the soap has removed the tannic acid.

The most remarkable compound of tannic acid, however, is that which it forms with *gelatin*, which constitutes the basis of *leather*. The principles of the manufacture of this important substance will be considered after the properties of gelatin have been described. When a solution of gelatin or isinglass is added to an aqueous infusion of any vegetable containing tannic acid, a copious gelatinous precipitate occurs, which is soluble in excess of gelatin if the liquid be boiled. An excess of tannic acid prevents the re-solution of the compound. If a piece of a raw hide freed from hair, be immersed in a solution of tannic acid, the gelatinous tissue gradually combines with the acid, and retains it in the form of leather, the supernatant liquid being ultimately completely freed from all traces of tannin, if the piece of skin be of sufficient size.

When gallotannic acid is subjected to a temperature of about 620°, it is decomposed, and yields pyrogallic and metagallic

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The essential constituents of catechu are mimotannic acid and catechin, which are mixed with a brown substance, resulting from the oxidation of both these bodies.

Mimotannic acid is sparingly soluble in dilute sulphuric acid, although freely soluble in water. If a concentrated aqueous infusion of catechu be mixed with a small quantity of dilute sulphuric acid, a precipitate occurs, at first consisting chiefly of colouring matter; this may be removed, and on then gradually adding concentrated sulphuric acid so long as it occasions a precipitate, mimotannic acid is thrown down: this precipitate may be collected on a filter, washed with dilute sulphuric acid, pressed between folds of blotting paper, and dissolved in water. The excess of sulphuric acid is then removed by digestion with carbonate of lead, and the filtered liquid, when evaporated *in vacuo*, furnishes mimotannic acid nearly pure.

This substance is distinguished from gallotannic acid, by yielding a greenish grey precipitate with the persalts of iron: and by not precipitating a solution of tartar emetic: when subjected to heat, it does not furnish pyrogallic acid. Its solution absorbs oxygen and becomes of a dark red colour, leaving, when evaporated, a substance no longer completely soluble in water. Under these circumstances, according to Delffs, a certain quantity of catechin is formed, and remains in a crystalline condition.

Catechin ($C_{20}H_9O_8$, HO; Zwenger) is contained in the portion of catechu which is not soluble in cold water: it is soluble in three or four parts of boiling water, or of boiling alcohol; and when pure is deposited in minute colourless crystals. The caustic alkalies immediately attack it, causing it to absorb oxygen, when it becomes first yellow, then red, and finally black. Catechin precipitates perchloride of iron of a dark green colour. It is soluble in the dilute acids: when treated with oil of vitriol it gives a purple solution: nitric acid converts it into oxalic acid. Catechin is fusible at 422°: at a higher temperature it is decomposed, and amongst other products yields a crystallizable substance termed *pyrocatechin*, or *oxyphenic acid* ($C_{12}H_6O_4$). *Moritannic acid* ($C_{36}H_{16}O_{10}$) (the tannin of the *morus tinctoria*, the yellow dye called *fustic*) yields the same product when submitted to distillation.

It has been suggested that the different varieties of tannic acid may be homologous terms of the same series; but the facility with which they undergo change renders their investigation a matter of great difficulty; and the accuracy of the formulæ assigned to these different compounds, with the exception of that of gallotannic acid, must be regarded as very doubtful.

7. *Gallic Acid, and its Derivatives.*

(1123) GALLIC ACID ($C_{14}H_6O_{10} + 2Aq = 3HO, C_{14}H_3O_7, 2Aq$).—This acid exists ready formed in the gall nut, in sumach, in valonia, and in a large number of other astringent vegetables, although the quantity in each is but small. It may readily be obtained by allowing an infusion of gall nuts, or the powdered galls moistened freely with water, to stand in a warm place for some weeks, exposed to the air: it quickly becomes mouldy, absorbs oxygen, and emits carbonic acid, owing to the occurrence of a species of fermentation, during which abundance of gallic acid is deposited in the form of crystals. The acid must be purified by digestion with animal charcoal and re-crystallization from boiling water. Gallic acid is also deposited from infusion of gall nuts, if kept in vessels from which air is excluded; but in this case no evolution of gas occurs: the exact stages of these processes of fermentation have not been clearly made out. Gallic acid may also be obtained by boiling tannic acid with dilute sulphuric or hydrochloric acid, in which case water is assimilated and glucose is set at liberty (1121).

The acid crystallizes either in the form of delicate silky needles, or in brilliant oblique rhomboidal prisms, which require about 100 parts of cold water for their solution, but only 3 parts of boiling water: they are freely soluble in alcohol, but only sparingly so in ether. When dried at 212° they lose 9·5 per cent., or 2 equivalents, of water.

Gallates.—According to Strecker, gallic acid is tribasic, and it forms three classes of salts, the general formulæ of which, are

$MO, 2HO, C_{14}H_3O_7$; $2MO, HO, C_{14}H_3O_7$; and $3MO, C_{14}H_3O_7$: besides these salts there are salts with an excess of acid, and with excess of base ; thus an acid salt of potash, $[2(KO, 2HO, C_{14}H_3O_7\ 3\,HO,)\ C_{14}O_3O_7, 2Aq]$ may be obtained by adding an alcoholic solution of potash to an alcoholic solution of gallic acid. The gallates of the alkalies speedily absorb oxygen, and become brown when their solutions are exposed to the air, especially if an excess of base be present. Nearly all the gallates of the heavy metallic oxides are insoluble. If an excess of gallic acid be added to a salt of lead, the precipitate is at first white and amorphous, but it gradually becomes crystalline if left in contact with the liquid. But the most characteristic reaction of this acid, is the formation a deep, bluish black solution, when added to a mixture of the protosalts and persalts of iron. If the solutions be free from acid, and particularly if a solution of bicarbonate of lime be added, the reaction is one of extreme delicacy. The salts of gallic acid do not cause a precipitate in solutions of gelatin.

When gallic acid is exposed to a temperature of from 410° to 420°, it is wholly volatilized, and is converted into pyrogallic and carbonic acids :—

$$3\ \overbrace{HO, C_{14}H_3O_7}^{\text{Gallic Acid.}} = \overbrace{C_{12}H_6O_6}^{\text{Pyrogallic Acid.}} + 2\,CO_2\,;$$

but if the temperature be allowed to reach 480°, the pyrogallic acid in its turn suffers decomposition; water is expelled, and a dark ulmin-like body is formed, termed *metagallic acid,* which is insoluble in water, but soluble in alkaline solutions :—

$$\overbrace{C_{12}H_6O_6}^{\text{Pyrogallic Acid.}} = \overbrace{C_{12}H_4O_4}^{\text{Metagallic Acid.}} + 2\ HO.$$

(1124) *Pyrogallic Acid* ($C_{12}H_6O_6$).—This substance possesses but very feeble acid properties. It may be obtained by the sublimation of gallic acid, or of any vegetable extract which contains gallotannic acid. The extract may be placed in a shallow iron pan, which is covered with a sheet of bibulous paper, over which a cone of writing paper is fastened; on applying a regulated sand heat, the pyrogallic acid is converted into vapour; it passes through the bibulous paper, and rises into the chamber formed by the paper cone, where it is condensed, and is prevented from falling back into the pan beneath, by the interposed sheet of filtering paper. This method of sublimation, contrived by Dr. Mohr, is applicable in many other cases of a similar kind.

Sublimed pyrogallic acid forms voluminous brilliant plates, which are freely soluble in water, alcohol, and ether: the solution has a very bitter taste, and does not redden litmus paper. When the acid is heated to about 240°, it melts; and when further heated, it emits a colourless, irritating vapour. The acid may be preserved unchanged whilst dry, but its solution quickly becomes brown, and absorbs oxygen; and if a free alkali be added, the absorption of oxygen is so rapid, as to afford a valuable method of removing free oxygen from gaseous mixtures (296 *note*).

The alkaline solutions of pyrogallic acid rapidly assume an intense reddish brown colour: this brown solution, according to Stenhouse (*Liebig's Ann.* xlv. 6), contains acetate and carbonate of the base. When the acid is dropped into milk of lime it produces a beautiful purplish red colour, which soon becomes of a dingy brown: this reaction is very characteristic. Pyrogallic acid, on account of the facility with which it absorbs oxygen, decomposes most of the salts of silver, of gold, and of platinum; but it forms a definite compound with oxide of lead, and dissolves freshly precipitated alumina. With protosulphate of iron, free from peroxide of this metal, it gives a deep indigo blue solution, which becomes green by the action of air: with persalts of iron it forms a bright red solution.

Pyrogallic acid is now extensively employed in photographic operations, for the purpose of developing the latent image upon the argentiferous collodion film after it has been exposed to the action of light (884).

(1125) *Ellagic Acid* ($HO, C_{14}H_2O_7$, 2Aq.; if dried at 240°, $HO, C_{14}H_2O_7$).—During the preparation of gallic acid from gall nuts, a quantity of a grey crystalline powder, termed *ellagic acid*, is formed: this substance is insoluble in water, but soluble in the alkalies: with potash it forms a flaky salt which is but sparingly soluble: the solution of this salt speedily absorbs oxygen from the air, and becomes of a blood-red colour. When treated with a solution of perchloride of iron, ellagic acid is gradually dissolved, and forms a deep blue liquid. The most singular circumstance in connexion with this body is the discovery of Wöhler and Merklein that it is a constituent of certain kinds of oriental bezoars. These bezoars are intestinal concretions which occur in the wild goats, antelopes, and deer of the countries of Central Asia: they are brittle, ovoid, or reniform masses of a dark olive-green colour, polished upon the surface, and in size seldom exceeding a pigeon's egg; when broken, they are usually found to have been deposited in concentric layers upon some foreign nucleus: they are not fusible like the lithofellic bezoars.

Concentrated sulphuric acid dissolves ellagic acid, and precipitates it, unaltered, on dilution.

Rufigallic or *Parellagic Acid* ($C_{14}H_4O_8$, 2Aq).—If the crystals of gallic acid be dissolved in five times their weight of oil of vitriol, a crimson solution is formed, which, if allowed to fall drop by drop into water, deposits a reddish-brown substance, partly in flocculi and partly in crystals. The crystalline portion, or *rufigallic acid*, is isomeric with ellagic acid: it is insoluble in water, but soluble in solutions of the alkalies. The acid, when heated, yields a sublimate consisting of fine red prisms, resembling those of alizarin. If a piece of calico which has been moistened with alum, or with a salt of iron, be boiled with rufigallic acid, it becomes dyed with the same tints as if madder had been used; but the colours are less brilliant than those of madder.

8. *Kinic Acid, and its Derivatives.*

(1126) KINIC ACID (2 HO, $C_{28}H_{20}O_{20}$; Gerhardt).—The bark of the cinchonas contains a peculiar modification of tannic acid, termed the quinotannic, and besides this, it furnishes the remarkable acid to which the name of *kinic* acid has been given. Kinic acid appears to exist in the bark in combination with lime and with the organic bases of the bark. If an aqueous decoction of cinchona bark be mixed with milk of lime until it assumes a feeble alkaline reaction, the vegetable bases and the tannic acid are precipitated, and kinate of lime remains in the liquid; this salt may be crystallized from the mother liquor by evaporation, and decomposed by means of oxalic or of sulphuric acid. The kinic acid may then be obtained in crystals from the solution.

Kinic acid crystallizes in colourless, oblique rhombic prisms, which have a strongly acid taste; they are freely soluble in boiling water, less so in cold water, still less so in alcohol, and very sparingly soluble in ether. When heated to 311° the acid fuses, and at a higher temperature yields a complicated mixture containing amongst other matters, benzole, benzoic acid, carbonic acid, salicylous acid, and a colourless substance termed hydrokinone.

Kinates.—Kinic acid appears to be dibasic; nearly all its salts are soluble in water, with the exception of the subkinate of lead (4 PbO, $C_{28}Pb_4H_{16}O_{20}$), which is obtained by adding a solution of subacetate of lead to a neutral kinate. It is remarkable that in this salt a portion of the hydrogen of the acid appears to have been displaced by lead. Kinic acid also forms a basic salt with copper ($4\,CuO,C_{28}H_{20}O_{20} + 8\,Aq$), which may be obtained in brilliant, green, sparingly soluble crystals.

(1127) *Kinone* ($C_{12}H_4O_4$).—When one part of kinic acid is heated with four parts of finely powdered peroxide of manganese and one part of sulphuric acid diluted with water, a beautiful yellow crystalline substance is sublimed, and condensed in the neck of the retort in long needles: to this substance the name of *kinone* has been given:—

$$\overbrace{2\,HO, C_{28}H_{20}O_{20}}^{\text{Kinic Acid.}} + O_8 = \overbrace{2\,(C_{12}H_4O_4)}^{\text{Kinone.}} + 4\,CO_2 + 14\,HO.$$

It may also be obtained from the aqueous extract of coffee by treating it in a similar manner. Kinone fuses at 212°. It is sparingly soluble in water, but is dissolved more freely by alcohol and ether.

Hydrokinone ($C_{12}H_6O_4$).—When kinone is treated with reducing agents, such as sulphurous acid or protochloride of tin, it is first converted into a green compound, but it ultimately furnishes a colourless body, termed *hydrokinone*. This substance is also the principal product of the dry distillation of kinic acid:—

$$\overbrace{2\,HO, C_{28}H_{20}O_{20}}^{\text{Kinic Acid.}} = \overbrace{C_{12}H_6O_4}^{\text{Hydrokinone.}} + \overbrace{HO, C_{14}H_5O_3}^{\text{Benzoic Acid.}} + 2\,CO_2 + 10\,HO.$$

But the simplest plan of preparing it consists in suspending kinone in water and transmitting sulphurous acid gas until the kinone is dissolved; by evaporating this solution, crystals of hydrokinone are obtained, whilst the liquid contains sulphuric acid. Hydrokinone forms six-sided, colourless prisms, which are very soluble in water, alcohol, and ether. It is without odour, and has a sweetish taste; it fuses readily, and may be sublimed in brilliant plates, resembling those of benzoic acid.

The action of oxidizing agents upon hydrokinone is remarkable. When its solution is mixed with a solution of sesquichloride of iron, the liquid immediately assumes a deep blackish-red colour, and in a few moments it becomes filled with magnificent green acicular crystals, which have a metallic lustre. These crystals consist of a combination of kinone with hydrokinone, which has been called *green hydrokinone*, ($C_{12}H_4O_4, C_{12}H_6O_4$). Chlorine, nitric acid, nitrate of silver, and chromate of potash, when mixed with a solution of hydrokinone, also occasion the formation of the same compound: the same substance is also formed by mixing a solution of kinone with one of hydrokinone. This beautiful compound fuses on the application of a gentle heat; it is partially decom-

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[illegible] important and vol[illegible] compounds which are obtained [illegible] from the animal and the vegetable kingdom. In [illegible] they present a close analogy with the com[illegible]. The predominating elements in their composition [illegible]gen, and as a general rule, the greater the pro[illegible] the less that of oxygen which they contain, the higher is their melting point. The vegetable fats and oils occur in various parts of the plant, but they are most abundant in the seed. The seeds of the *cruciferæ* are particularly remarkable for the large quantity of oil which they furnish; rapeseed contains from 35 to 40 per cent. of oil, and linseed furnishes more than a fifth of its weight. The fleshy fruit of the olive also yields oil in great abundance, and the same is the case with the *Elais guineensis* or palm oil fruit. In animals, fat is particularly liable to accumulate immediately beneath the cuticle, also in the omentum and around the kidneys. The fatty bodies obtained from warm-blooded animals are generally solid at ordinary temperatures; whilst those from fish and from cold-blooded animals are liquid. In all cases, both in the animal and in the plant, a certain quantity of some albuminoid substance occurs associated with the oily body, and this substance exerts an important chemical influence upon the fat when kept. In the extraction of the oil, simple pressure is generally sufficient to separate it from the cells of the tissue in which it is contained. If it be solid at ordinary temperatures, it may often be procured by boiling the tissue with water; it then rises to the surface and forms a layer which solidifies on cooling.

The fats and oils are lighter than water, having a specific gravity varying from about 0·91 to 0·94; they have different degrees of solidity, and do not consist of any single proximate principle in a state of purity, but are for the most part mixtures, in varying proportions, of at least three different closely allied bodies; two of which, viz., *stearin* (from *στέαρ*, suet) and *margarin* (from *μάργαρον*, a pearl, owing to its pearly lustre), are solid at ordinary temperatures; whilst the third, *olein*, is liquid. The larger the proportion of olein which is present, the softer is the fat, and the lower is its fusing point.

All fats are soluble in ether, and to a certain extent also in alcohol. Oil of turpentine and benzole likewise dissolve them with facility, and the different fats and oils may be mixed with each other in all proportions. They possess the property of rendering paper semitransparent, producing what is well known as a greasy stain. The fats and oils may be heated to nearly 500° without undergoing any important change, but they cannot be distilled without experiencing decomposition. Hence the term, *fixed oils*, is applied to these bodies in contradistinction to that of *volatile oils*, which is given to the fragrant essences obtained from the vegetable kingdom, which may be distilled without alteration. At about 500° the fats and oils begin to give off acrid and offensive vapours, and at a little above 600°, they are rapidly decomposed with evolution of gaseous hydrocarbons, the escape of which gives to the oil the appearance of ebullition; as the result of the distillation, a mixture of solid and liquid hydrocarbons, of water and of various fatty acids, accompanied by a peculiarly irritating substance termed acrolein (1151), are condensed in the receiver.

(1129) *General Nature of the Neutral Fats.*—The fatty bodies when heated with the hydrated alkalies, experience a peculiar change, long known under the title of *saponification,* or conversion into soap (1143), during which process all fats yield up a viscid liquid, which, owing to its sweet taste, has been termed *glycerin* (from γλυκὺς, sweet). The nature of this change may be ascertained by dissolving the soap in water, and then adding some acid, such as the tartaric or the hydrochloric, which combines with the alkali and forms a soluble compound with it. Unctuous flocculi are thus separated, and on the application of heat they melt, and form an oily layer on the surface of the fluid. This substance when cold is found to possess properties very different from those of the original fat. It is crystalline, freely soluble in alcohol, and the spirituous solution reddens litmus paper strongly. It possesses distinctly acid characters, and it is soluble at once, and without the appearance of milkiness, in hot alkaline liquids.

This unctuous matter varies in consistence and quality with the nature of the fat from which it is procured, and is for the most part a mixture of three acids (derived from the three bodies already mentioned as forming the greater number of the fats), and termed respectively, *oleic, stearic,* and *margaric* acids. It is found that the united weight of the glycerin and of these fatty acids, always exceeds by three or four per cent. that of the fat originally employed.

In fact, the olein, stearin, and margarin are each compounds of their respective fatty acid, with the basis of glycerin, which has been displaced by the alkali in the act of forming soap; the alkali in displacing the base of the glycerin, gives up a portion of water to it, and hence increases its weight; while the fatty acid, on being separated from the soap, also in like manner combines with a portion of water. Simple mixture of the glycerin and of the fatty acid together, therefore, does not again produce the oil or fat from which they were obtained.

Notwithstanding the numerous researches which have been made upon saponification, the exact formula for the neutral fats such as stearin, is still a matter of doubt, and the proportion of water which is absorbed during their saponification is uncertain. The neutral fats, however, are evidently analogous in composition to the compound ethers, and as these by the action of water become converted into the hydrated acid and alcohol, so the fats are by saponification, or by the action of water at an elevated temperature, converted into the hydrated fatty acid, and glycerin. Oxalic ether, for instance, undergoes the following decomposition :—

$$\overbrace{2\,C_4H_5O,\,C_4O_6}^{\text{Oxalic Ether.}} \;+\; 4\,HO \;=\; \overbrace{2\,(C_4H_5O,\,HO)}^{\text{Alcohol.}} \;+\; \overbrace{2\,HO,\,C_4O_6}^{\text{Oxalic Acid.}};$$

and the formation of stearic acid and glycerin from stearin, may be represented by an analogous equation ; thus :—

$$\overbrace{C_{114}H_{110}O_{12}}^{\text{Stearin.}} \;+\; 6\,HO \;=\; \overbrace{C_6H_8O_6}^{\text{Glycerin.}} \;+\; \overbrace{3\,(HO,\,C_{36}H_{35}O_3)}^{\text{Stearic Acid.}}.$$

When the oils are mixed with an aqueous solution of the alkalies, saponification takes place slowly, but if the oil be dissolved in alcohol, and then mixed with an alcoholic solution of the caustic alkali, both at a boiling temperature, the saponification is instantaneous and complete.

Pelouze has recently shown that the saponification of the fats and oils may be effected by heating them with the anhydrous bases, such as caustic lime and oxide of lead ; but a large proportion of the glycerin is always destroyed in the operation, for want of water with which it can combine at the moment of its liberation from the fat ; and unless the heat be carefully regulated, the fatty acid itself is liable to become decomposed.

When the oily seeds, such as almonds, walnuts, or poppy seeds, are crushed or pulverized, so as to break up the cellular tissue, and bring its several components into mixture with each other, the neutral fatty bodies which the seeds naturally contain are gradually converted into fatty acids, and glycerin is liberated. This change has been shown by Pelouze to depend upon the action of an albuminous ferment contained in the pulp, and is independent of any absorption of oxygen.

The fats are more fusible than the acids which they furnish on saponification, but when exposed to a low temperature they become much harder than the fatty acids. Generally they are destitute of odour and taste ; the peculiar scent emitted by some of them depending upon the presence of a small proportion of some glycerin compound of one of the volatile oily acids, such as the butyric, valeric, or rutic. It is worthy of remark, that although the fats themselves are but sparingly soluble in alcohol, their solubility is greatly increased by the presence of a free fatty acid. Ammonia appears to combine with many of the oils, but it converts them into amides, and not into true soaps (Rowney). The compounds of ammonia with almond oil and with castor oil are crystalline.

(1130) *Rancidity of Oils.*—Fats and oils are subject to a peculiar change in their properties, popularly distinguished by the term "rancidity." This change is attended with a slight absorption of oxygen, and it appears to be due to the decomposition of certain mucilaginous and albuminous matters contained in the oil, which during their decay react on the fat, setting free the fatty acids, and decomposing the glycerin. Perfectly pure fats and oils do not become rancid, and rancidity may be completely removed by melting or washing them first with boiling water, and subsequently with a cold weak alkaline ley. When the vegetable oils are employed for purposes of illumination, it is necessary to purify them from these mucilaginous matters, which otherwise become charred and encrust the wick, and thus prevent the oil from burning freely. To effect this purification, the oil may be mixed with one-fiftieth of its weight of oil of vitriol, which is to be added in small portions at a time, keeping the mixture in continual agitation; dark flocculi are thus formed, which subside when the mixture is left at rest. The supernatant oil is then to be drawn off, and the adhering acid is to be removed by agitating it with one-fourth its volume of water, mingled with a small proportion of lime. Lastly, the oil is rendered fit for use by filtration through charcoal.

(1131) *Drying and Non-drying Oils.*—Oils may be further arranged under two distinct classes, according as they possess or do not possess the property of absorbing oxygen, by which they are gradually converted into a solid mass; those which become solid in this manner, are termed *drying oils.* Some oils, such as linseed oil, in undergoing this change do not evolve any gas; but during the solidification of most others, an evolution of carbonic acid, attended sometimes with an escape of hydrogen, takes place.

The non-drying oils do not absorb oxygen, but are converted into elaidin by means of subnitrate of mercury or by peroxide of nitrogen, a reaction of which those of the first variety are not susceptible. The solidification of olive oil is effected by a quantity of NO_4, not exceeding $\frac{1}{200}$th of the weight of the oil (1177).

The principal drying oils are those of linseed, walnut, hemp, poppy, cod liver, and sperm oil. The absorption of oxygen by some of these oils, and consequent elevation of temperature, is, under favourable circumstances, so rapid as to be attended with heat sufficient to cause the mass to take fire; and several serious conflagrations have been traced to the spontaneous ignition of cotton wool or tow soaked in linseed oil, which had been thrown aside in refuse heaps after it had been used in cleaning machinery. The siccative or drying property of these oils may be much increased by heating them with about one-twentieth of their weight of litharge, which becomes completely dissolved by the oil. Oxide of manganese may be used for the production of a similar effect: linseed oil which has been thus treated, is technically known as *boiled oil*. Chevreul, however, states that it is unnecessary to heat the oil for so long a time, or to so high a temperature as is commonly practised; linseed oil heated to 140° in contact with one-tenth of its weight of oxide of manganese, having acquired powerful siccative properties. According to Liebig, the increased rapidity with which oil thus treated becomes hard on exposure to the air, is due to the mechanical removal of the impurities of the oil by the oxide of lead, which allows the oxygen to come more freely into contact with each particle of the oil.

The drying oils are not solidified by contact with peroxide of nitrogen, or with subnitrate of mercury, and a fraudulent mixture of them with olive or almond oil may thus be detected. The oleic acid which they furnish on saponification, differs from ordinary oleic acid, and absorbs oxygen much more rapidly than the latter; and in consequence of this oxidation it speedily becomes converted into a transparent solid varnish. For a careful investigation of the changes which occur during the drying of oils, the reader is referred to a paper by Chevreul (*Ann. de Chimie*, III. xlvii. 209). The most important of the oils which do not become dry by exposure to the air are olive oil, almond oil, rape oil, and colza oil, besides many animal oils.

(*a*) *Composition and Properties of the principal Oils and Fats.*

(1132) 1. *Olive oil* is prepared in great abundance in the southern countries of Europe; it furnishes the principal oily material employed in making Marseilles and Castile soap. The ripe olives are first subjected to pressure without the application of heat; in this manner the finest oil, or *virgin oil*, is obtained: the residue is afterwards heated with water, and a large quantity of an inferior mucilaginous oil rises to the surface; it is this which is chiefly employed in soap-making. The oil is always of much finer quality if extracted immediately after the fruit has been crushed, as otherwise it experiences a kind of fermentation, which injures the quality of the product. The solid ingredient in olive oil is almost exclusively margarin. Olive oil soon becomes rancid when kept; it becomes partially solid at a few degrees below 32°. It has the sp. gr. 0·918.

2. *Almond oil* is much less extensively employed; it is extracted from the kernel of the *amygdalus communis*, by a process similar to that adopted for olive oil. It has the specific gravity 0·918 at 60°, and solidifies at about —13°.

3. *Colza oil*, which is largely used for illuminating purposes, is obtained from the seeds of the *brassica oleifera*. It is of a yellow colour, and is nearly free from odour. It has the sp. gr. 0·913. At a temperature of 22° F. it becomes nearly solid. Colza oil is sparingly soluble in cold alcohol, but is readily dissolved by this liquid with the aid of heat.

4. *Linseed oil* is pressed from the seeds of the *linum usitatissimum*, which yield about one-fifth of their weight of it. It has a slight peculiar odour, is of a yellow colour, and has the sp. gr. 0·939 at 54°. It remains liquid till within a few degrees of 0°. Owing to its powerful drying properties, which are much increased after boiling with a small quantity of litharge or of peroxide of manganese, it is extensively used as a vehicle for mixing with colours for painting in oil: it is also largely employed in the preparation of printer's ink, in the preparation of black enamel for leather, and in the varnishing of oiled silk. If exposed for some time to a high temperature it becomes converted into a dark tenacious mass, which when cold may be drawn out into threads; in this state, if mixed with charcoal, it constitutes printer's ink. If the tenacious residue obtained by heating the oil be boiled for some hours with dilute nitric acid, it acquires a consistence resembling that of ordinary lead plaster, and becomes hard on exposure to the air, but it softens again by the heat of boiling water, and acquires a consistence resembling that of caoutchouc, for which it has been substituted in some instances. This *caoutchouc of oils* is soluble in oil of turpentine, in bisulphide of carbon, and in dilute alkaline solutions; on neutralizing these alkaline solutions of the caoutchouc by means of an acid, the caoutchouc is precipitated unaltered. Other drying oils besides linseed oil, yield a similar substance, though less abundantly.

The oleic acid furnished by the saponification of linseed oil differs from ordinary oleic acid; Sacc terms it *linoleic acid*, and assigns to it the formula ($HO, C_{46}H_{48}O_5$). It absorbs oxygen rapidly from the air, even when combined with oxide of lead and other bases.

5. *Sperm oil* is the liquid portion of the fat of the spermaceti whale. It has the sp. gr. 0·868, and is of a yellow colour; it has a peculiar disagreeable odour and taste, due to the presence of a small quantity of a peculiar oil, termed *phocenin* by Chevreul; this body when saponified yields glycerin and a volatile acid, apparently identical with the valeric. The other constituents of the oil are margarin and olein. The olein contained in sperm oil differs from that of olive oil, since, although it becomes solid under the action of peroxide of nitrogen, it possesses a drying quality. Sperm oil becomes semisolid at about 45°. It may be purified by agitating 100 parts of the oil with a mixture of 4 parts of chloride of lime with 12 of water; a small quantity of decoction of oak bark is afterwards added to remove traces of a gelatinous matter which it retains, and the mixture is left to settle; the clear oil is afterwards agitated with a small proportion of sulphuric acid, again clarified by subsidence, and washed to remove adhering sulphuric acid.

6. Ordinary *whale oil* is of a darker yellow colour, and has a more disagreeable odour than the foregoing oil. It has the sp. gr. 0·927, and does not become solid above 32°.

7. *Cod liver oil* has recently acquired importance from its extensive employment as a therapeutic agent. It is extracted from the liver of the *Gadus morrhua*, or common cod fish. Its colour varies from a pale, scarcely perceptible yellow, to a deep brown, according to the mode of its extraction. It has a peculiar fishy odour and taste, and the sp. gr. 0·928. In addition to the usual components of the fish oils, it appears to contain a compound of acetic acid with glycerin (acetin, 1149); it also contains a certain proportion of the constituents of the bile, and a small quantity of a phosphorized fat, besides minute quantities of iodine and bromine in a state of combination with some organic substance. Ether dissolves the oil without difficulty, but cold alcohol takes up only a small quantity of it. The iodine and bromine are not in the form of a metallic iodide or bromide; indeed, their presence cannot be detected until the oil has been saponified and the soap charred. When a drop of concentrated sulphuric acid is allowed to fall into the oil, it produces a beautiful crimson colour, owing to the action of the acid upon the biliary matter present.

8. *Castor oil* (*sp. gr.* 0·969, obtained from the seeds of the *Ricinus communis*) forms a connecting link between the drying and non-drying oils, since it gradually becomes hard by long exposure

to air. Castor oil has an acrid taste, which it is stated may be removed by agitation with magnesia. This oil is of a very viscid consistence, but it does not become solid even at a temperature of 0° F. Castor oil differs from the other fixed oils in being soluble in alcohol in all proportions. The principal acid obtained by its saponification is a modification of oleic acid, termed *ricinolic* acid ($HO, C_{36}H_{33}O_5$), which remains fluid at a temperature considerably below 32°. By the action of peroxide of nitrogen it becomes converted into a solid isomeric fat, termed *ricinelaidic* or *palmic* acid. When treated with ammonia, castor oil yields a solid crystalline amide, *ricinolamide* ($C_{36}H_{35}NO_4$). The oil, when distilled, furnishes œnanthylic acid ($HO, C_{14}H_{13}O_3$; 1161), and a large quantity of the aldehyd of this acid ($C_{14}H_{14}O_2$; 977), which was termed œnanthol by Bussy. When castor oil is distilled with hydrate of potash it is decomposed, the principal products being sebacic acid (1179), which remains in the retort, whilst hydrogen gas is liberated, and a quantity of a volatile liquid, octylic or caprylic alcohol, is distilled over (969).

(1133) *The Solid Fats.*—The solid fats of vegetable origin which are in most frequent use are cocoa-nut oil, nutmeg butter, and palm oil; those of animal origin are butter, suet, lard, spermaceti, and bees' wax.

Palm oil, nutmeg butter, and cocoa-nut oil, each contain a different solid fatty acid, which, in combination with the basis of glycerin, constitutes the principal portion of the solid part of the oil.

1. *Cocoa-nut oil* is obtained from the *Cocos nucifera*. It is largely consumed in the manufacture of candles; it is also used in the preparation of a species of soap employed for washing in sea water, and hence termed *marine* soap; it fuses at about 68°. Cocoa-nut oil is a very complex fat, for it yields not fewer than six different acids on saponification. These acids, according to Georgey, are—

Caproic acid	. $HO, C_{12}H_{11}O_3$	Lauric acid	. $HO, C_{24}H_{23}O_3$
Caprylic acid	. $HO, C_{16}H_{15}O_3$	Myristic acid	. $HO, C_{28}H_{27}O_3$
Rutic acid	. $HO, C_{20}H_{19}O_3$	Palmitic acid	. $HO, C_{32}H_{31}O_3$.

Cocoa nut oil probably also contains oleic acid, since it yields sebacic acid when distilled.

2. *Palm oil* is produced from the pulp of the ripe fruit of the *Elais guineensis*, which is of a bright orange or golden yellow colour. The oil is obtained by heating the crushed fruit with

boiling water. It has an agreeable odour resembling that of violets. The solid portion of palm oil consists chiefly of a peculiar fat, which has received the name of palmitin, and which, when saponified, yields palmitic acid ($HO, C_{32}H_{31}O_3$). Palm oil speedily becomes rancid when kept, and, though when fresh it melts at about 81°, it gradually becomes less fusible till it remains solid at a temperature of 100°. This change is due to the spontaneous decomposition of the palmitin, and the liberation of palmitic acid, under the influence of the azotised constituent of the fruit which accompanies the oil in the process of extraction. Palm oil is readily decolorized by exposure to air at a high temperature, but it is more usual to effect this bleaching of the oil by the addition of a small quantity of sulphuric acid and bichromate of potash. This oil constitutes an important article of commerce, upwards of 20,000 tons being annually imported from the western coast of Africa. It is consumed in immense quantities in the manufacture of candles and of soap.

3. *Butter* consists of a mixture of several fats, amongst which palmitin is the principal solid constituent; the olein was considered by Bromeis to be of a peculiar kind, which he termed *butyrolein;* but Gottlieb has shown that the difference in properties between the oleic acid obtained by Bromeis from butter, and that obtained from ordinary olein, depended simply upon the oxidation which it had undergone during the process adopted in preparing it; and he has procured pure oleic acid from butter. According to Heintz, the solid portion of butter contains, in addition to palmitic acid, another acid, termed by him *butic acid,* $HO, C_{40}H_{39}O_3$. The characteristic odour and flavour of butter are owing to the presence of a small quantity of some peculiar fats, viz., butyrin, caproin, and caprylin; each of these fats, when saponified, yields glycerin, and a peculiar volatile acid, viz., butyric acid $HO, C_8H_7O_3$, caproic acid $HO, C_{12}H_{11}O_3$, and caprylic acid $HO, C_{16}H_{15}O_3$.

In certain instances Lerch found no butyric or caproic acid in butter, but in their stead he discovered an acid, which he has termed the *vaccinic* ($HO, C_{20}H_{19}O_5$). This acid contains the elements of 1 equivalent of hydrated butyric acid and one of hydrated caproic acid, minus 2 equivalents of oxygen:—

$$\overbrace{HO, C_{20}H_{19}O_5}^{\text{Vaccinic Acid.}} + 2\,O = \overbrace{HO, C_8H_7O_3}^{\text{Butyric Acid.}} + \overbrace{HO, C_{12}H_{11}O_3}^{\text{Caproic Acid.}}.$$

A solution of vaccinate of baryta, when exposed to the air, absorbs oxygen, and thus becomes converted into a mixture of butyrate and caproate of this base.

4. *Lard* is the soft fat of the pig, in which the olein predominates over the margarin and stearin.

5. *Suet* is the fat of the ox or of the sheep; when melted down it forms tallow. Mutton suet is of a firmer consistence than that from the ox; its solid portion consists almost exclusively of stearin.

(1134) SPERMACETI is the solid crystalline fat which is extracted from the brain of the spermaceti whale; it is accompanied by a fluid oil (sperm oil). Spermaceti differs from the ordinary fats in not yielding glycerin when saponified, but in furnishing in its stead a different base, termed *ethal* ($C_{32}H_{34}O_2$). Pure spermaceti, or *cetin* ($C_{64}H_{64}O_4$), fuses at about 120°, and solidifies to a silky semitransparent crystalline fat of delicate whiteness, and of the sp. gr. ·940. It is insoluble in cold alcohol of sp. gr. of ·816, but is soluble in hot anhydrous alcohol, and is freely soluble in hot ether, from which it crystallizes on cooling. It is acted on with difficulty by an aqueous solution of potash. If subjected to distillation, it is decomposed; a liquid hydrocarbon, $C_{32}H_{32}$, called *cetene* or *cetylene*, passes over, and ultimately palmitic acid (the ethalic of Dumas) ($HO, C_{32}H_{31}O_3$) distils over.

The same acid is formed when spermaceti is fused with hydrate of potash at a heat of about 220°. Under these circumstances, the mass, which is at first fluid, gradually solidifies. When this has occurred, it must be treated with water, and decomposed by hydrochloric acid: the fatty mass is boiled with lime, and then treated with alcohol; palmitate of lime remains undissolved, whilst the new fatty base, ethal, is recovered by evaporation. It is purified by redissolving it in ether and evaporating.

Ethal ($C_{32}H_{34}O_2 = C_{32}H_{33}O, HO$) is a white solid, fusible at 118°. It is soluble in hot alcohol, and crystallizes in plates as it cools. It may be volatilized by heat without experiencing decomposition. If distilled with anhydrous phosphoric acid, it yields *cetene* $C_{32}H_{32}$, a hydrocarbon homologous with olefiant gas. Ethal possesses the properties of a true alcohol; it stands in the same relation to palmitic acid as alcohol does to acetic acid; for example:—

$$\overbrace{C_4H_5O, HO}^{\text{Alcohol.}} + O_4 = \overbrace{HO, C_4H_3O_3}^{\text{Acetic Acid.}} + 2\,HO;$$

$$\overbrace{C_{32}H_{33}O, HO}^{\text{Ethal.}} + O_4 = \overbrace{HO, C_{32}H_{31}O_3}^{\text{Palmitic Acid.}} + 2\,HO.$$

When the vapour of alcohol is passed over heated hydrate of potash, hydrogen escapes, and acetate of the base remains behind; whilst ethal, under similar treatment, also evolves hydrogen, and produces palmitate of potash:—

$$\overbrace{C_4H_5O,\ HO}^{\text{Alcohol.}} + \overbrace{KO,\ HO}^{\text{Hydrate of Potash.}} = \overbrace{KO,\ C_4H_3O_3}^{\text{Acetate of Potash.}} + H_4;$$

$$\overbrace{C_{32}H_{33}O,\ HO}^{\text{Ethal.}} + \overbrace{KO,\ HO}^{\text{Hydrate of Potash.}} = \overbrace{KO,\ C_{32}H_{31}O_3}^{\text{Palmitate of Potash.}} + H_4.$$

With sulphuric acid it forms a coupled acid, the *sulphocetic*, ($HO,\ C_{32}H_{33}O,\ 2\ SO_3$), which corresponds with sulphethylic acid. A *cetylic ether* $2\ (C_{32}H_{33}),\ O_2$ has also been obtained, spermaceti being, in fact, a compound of this body with palmitic acid, or a palmitate of oxide of cetyle $(C_{32}H_{35})O,\ C_{32}H_{31}O_3$, and a homologue of acetic ether $(C_4H_5)O,\ C_4H_3O_3$. Spermaceti, when oxidized by nitric acid, yields œnanthylic, adipic, and pimelic acids, and a large quantity of succinic acid.

(1135) BEES' WAX has been the subject of numerous investigations, but its true nature appears at length to have been satisfactorily explained by Brodie (*Phil. Trans.*, 1848, 1849). Many vegetables produce substances in appearance greatly resembling the wax furnished by the honey-bee, but these bodies have not been thoroughly examined. Bees, even though fed upon pure sugar only, have the power of converting it into wax, which is therefore to be regarded in the light of an animal secretion. Bees' wax, at ordinary temperatures, is tough and solid: it has a yellow colour, a peculiar smell, and an unctuous feel; it fuses at about 145°, and has the sp. gr. 0·96. When exposed in thin slices to the air it becomes bleached, and is then somewhat less fusible. It may also be bleached by means of nitric acid; but chlorine, though it destroys the colour, cannot be employed for this purpose with advantage; for it was observed by Gay Lussac that a substitution of chlorine for a portion of hydrogen occurs under these circumstances, and when candles made from such wax are burned, irritating vapours of hydrochloric acid are evolved.

Wax consists of three different substances, which may be partially separated from each other by means of alcohol. These bodies are, 1. *Myricin*, which is insoluble in boiling alcohol; 2. *Cerin*, or cerotic acid, which is dissolved by boiling alcohol, but crystallizes out on cooling, and, 3. *Cerolein*, which is retained in the cold alcoholic liquid.

Cerolein, the substance soluble in cold alcohol, is a greasy body, to which the colour, odour, and tenacity of the wax are due; it has an acid reaction; it fuses at about 83°, and is readily soluble in ether; but it has been only incompletely examined. It constitutes not more than 4 or 5 per cent. of the wax.

Cerotic acid ($HO, C_{54}H_{53}O_3$; Brodie) is extracted from wax by means of boiling alcohol, and is purified by recrystallization from alcohol until its melting point rises to 162° F. It is then recrystallized from ether until it fuses at 174°, which is the melting point of the pure acid. The proportion of free cerotic acid contained in wax varies in different samples. In a specimen from Ceylon it was entirely wanting. In a sample of genuine bees' wax, operated on by Brodie, the cerotic acid constituted about 22 per cent. of the wax.* If due care be taken, cerotic acid may be distilled without undergoing decomposition.

Myricin.—The portion of the wax insoluble in alcohol constitutes upwards of two-thirds of the bulk of ordinary bees' wax. It melts at 147°. It is a mixture of two different bodies, both of which are insoluble in alcohol, but soluble in ether; a portion crystallizes from the ethereal solution in feathery scales; by repeated crystallization from ether a substance may be obtained, which solidifies at 162° F. To this substance the name of myricin is confined by Brodie. The other more fusible body which accompanies it is less abundant, and has not been completely investigated. Purified myricin, when treated with hydrate of potash, is easily saponified; by this means a salt of palmitic acid is obtained, and another wax alcohol, *melissylic* alcohol, or *melissin*, ($C_{60}H_{61}O, HO$), is liberated. From this decomposition it appears that myricin is a body analogous to spermaceti and to Chinese wax; pure myricin being a *palmitate of oxide of melissyle*, ($C_{60}H_{61}O, C_{32}H_{31}O_3$) or ($C_{92}H_{92}O_4$).

Melissin fuses at 185°. It is soluble with difficulty even in boiling alcohol. It crystallizes from a hot solution in ether in satiny crystals. Benzole is a better solvent for it than either alcohol or ether. When melissic alcohol is distilled with heated hydrate of potash, it is decompossd, hydrogen is evolved, and melissate of potash is formed; the reaction being analogous to that

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* Chinese wax, ($C_{108}H_{108}O_4$), the produce of a species of insect of the coccus tribe, contains cerotic acid in a state of combination with oxide of cerotyle, forming a substance which fuses at 182°, and is homologous with spermaceti, which in its crystalline appearance it considerably resembles:—

$$\overbrace{(C_{32}H_{33})O, C_{32}H_{31}O_3}^{\text{Spermaceti.}} \quad ; \quad \overbrace{(C_{54}H_{55})O, C_{54}H_{53}O_3}^{\text{Chinese Wax.}}$$

Chinese wax, when decomposed by fusion with hydrate of potash, yields cerotate of potash, and at the same time *cerotin*, ($C_{54}H_{55})H, O_2$, the alcohol of cerotic acid (corresponding to the ethal of spermaceti) is obtained.

by which acetate of potash is produced when ordinary alcohol is treated in a similar manner:—

$$\overbrace{C_{60}H_{61}O, HO}^{\text{Melissin.}} + KO, HO = (\overbrace{KO, C_{60}H_{59}O_3}^{\text{Melissate of Potash.}}) + H_4 .$$

Melissic acid, it will be seen, is the homologue of acetic acid, and belongs to the series of acids, $HO, (C_nH_{n-1})O_3$; it fuses at 192° F., and may be volatilized without decomposition.

Wax, when submitted to distillation, yields several solid hydrocarbons, among which is *melene* ($C_{60}H_{60}$). The principal product of the oxidation of wax by means of nitric acid is succinic acid.

From the foregoing statements it appears, therefore, that bees' wax is a mixture of cerotic acid (cerin) with palmitate of melissyle (myricin), in addition to which is a portion of a third body allied to myricin, as yet but imperfectly examined; with a small quantity of a soft greasy substance, cerolein. The following substances may be enumerated as derivatives from wax:—

Cerotic acid (*cerin*) . .	$HO, C_{54}H_{53}O_3$
Cerylic alcohol (*cerotin*) .	$C_{54}H_{55}O, HO$
Chinese wax . . .	$C_{108}H_{108}O_4$
Cerene (*paraffin*) . .	$C_{54}H_{54}$
Melissylic alcohol (*melissin*) .	$C_{60}H_{61}O, HO$
Melissic acid . . .	$HO, C_{60}H_{59}O_3$
Palmitic acid . . .	$HO, C_{32}H_{31}O_3$
Myricin	$C_{92}H_{92}O_4$
Melene (*paraffin*) . .	$C_{60}H_{60}$.

(*b*) *Proximate Constituents of the Fats and Oils.*

(1136) From the preceding general description of the oils and fats, it is evident that these bodies contain several distinct substances, which are analogous to each other in chemical composition. The most important of these neutral fats are stearin, palmitin, margarin, and olein.

(1137) STEARIN ($C_{114}H_{110}O_{12}$; Berthelot) is a white crystalline fat, soluble in about seven times its weight of boiling alcohol, and much more freely so in hot ether. Nearly the whole of the stearin separates from these liquids as they cool. Duffy (*Q. J. Chem. Soc.*, v. 210) finds that stearin may exist in three modifications, each of which has a different fusing point. Under ordinary circumstances, the melting point is 144° F., but this temperature varies in a remarkable manner under the influence of slight differences of the temperature to which the stearin is exposed during the act of fusion:—1. If stearin be heated to 151°, and allowed to cool, it remains liquid till it reaches 124°, and after solidification it may be melted at 125°·6;—2. but if stearin, which has been melted at this temperature, be again allowed to solidify, it requires a temperature of 147°·4 for its liquefaction;—and 3. stearin, which has been melted at 144°, and the temperature of which has not been raised beyond 147°, solidifies at 141°·8, but after solidification it requires a temperature of 157° for its liquefaction. These three modifications of stearin have different densities:—

	Sp. Gr.
1. Modification *a*, fusible at 125°·6 .	0·986
2. Modification *β*, fusible at 147°·4 .	1·010
3. Modification *γ*, fusible at 157° .	1·017*

Similar modifications are produced by heat upon palmitin.

Stearin is the most abundant of the solid constituents of the fats and fixed oils. It is generally prepared from mutton suet, in which it is mixed with but small quantities of other fats: the suet is heated with about ten times its volume of ether; when it cools, the olein and margarin are held in solution, while the stearin crystallizes in pearly scales. These must be pressed between folds of blotting paper, redissolved in ether, and recrystallized until the melting point becomes constant.

Berthelot has succeeded in preparing stearin artificially, by heating stearic acid and glycerin together in closed vessels for several hours under pressure. He has also obtained all the other neutral fats by similar means (1149).

(1138) PALMITIN ($C_{102}H_{98}O_{12}$; Berthelot).—This fat is contained abundantly in palm oil, from which it has received its name. It is extracted from the oil by first pressing out the liquid portion, treating the residue with boiling alcohol to remove free palmitic acid, and then crystallizing repeatedly from ether. According to Duffy the lowest point at which palmitin remains liquid is 113°·9; but it has three different melting points, viz.—114°·8, 143°, and 145°, which correspond to three different modifications like those of stearin. Palmitin is also present in bees'-wax, in cocoa-nut oil, and (according to Heintz) in human fat. The tree wax of Japan, according to Sthamer, consists of pure palmitin.

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* Heintz, on repeating Duffy's experiments upon pure stearin prepared synthetically by Berthelot's process (1149), obtained only the varieties *a* and *γ*; Duffy's *β* he considers to have been produced from the presence of a slight impurity in the stearin. The fusing points given by Heintz are a little higher than those of Duffy—viz., for *a* 131°, and for *γ* 160°·8.

(1139) **Margarin** ($C_{108}H_{104}O_{12}$; Berthelot) crystallizes in pearly scales, which are fusible at about 116°. It requires about 400 times its weight of boiling alcohol for solution, and is deposited almost entirely on cooling. Margarin constitutes the solid ingredient of goose grease, of human fat, and of olive oil. It may be extracted from olive oil by cooling it to 32°, and then submitting it to pressure; the solid portion is again melted and cooled slowly, and a second time submitted to pressure, at a temperature of from 55° to 60°. After two or three crystallizations from boiling alcohol, the margarin is obtained nearly pure.

According to Heintz, margarin is not a simple fat; for when saponified, the acid which it yields, and which is commonly described as margaric acid, admits of separation into palmitic and stearic acids; hence what is called margaric acid appears to be a mere mixture of these acids (1156).

(1140) **Olein** ($C_{114}H_{104}O_{12}$; Berthelot).—Pure olein is colourless; it is not solidified by a cold of 32°. By exposure to the air it absorbs oxygen slowly, with evolution of carbonic acid, and becomes resinoid in appearance. Olein when distilled gives rise, amongst other products, to the formation of sebacic acid ($2\,HO, C_{20}H_{16}O_6$), which is a characteristic product of the destructive distillation of oleic acid. Peroxide of nitrogen converts olein into an isomeric solid fat, which has received the name of *elaidin*. Subnitrate of mercury, which has been prepared without the aid of heat, retains a sufficient quantity of peroxide of nitrogen to enable it, when placed in contact with olein, to convert it into elaidin; and it produces a similar effect upon all oils which contain that variety of olein which is present in the non-drying oils. The drying oils contain a form of olein which does not become solid when mixed with subnitrate of mercury; hence this salt has been employed in testing olive oil suspected to have been adulterated with poppy and other cheap drying oils. The oil is agitated with $\frac{1}{12}$th of its weight of a solution of the sub-nitrate; the purer the oil the more readily does it become solid when thus treated.

The purification of olein is attended with considerable difficulty: it may however be obtained either by solidifying olive oil at a temperature of 32° and pressing out the liquid portion, or by dissolving the oil in boiling alcohol, which, as it cools, deposits nearly the whole of the stearin and margarin, but retains the whole of the olein in solution: the olein may then be recovered by driving off the alcohol by heat. Olein is saponified with greater difficulty than the solid fats which accompany it, and it has been proposed to apply this circumstance to its purification. If olive oil be boiled for twenty-four hours with solution of caustic soda of moderate strength, containing a quantity of alkali equal to about half that required for the complete saponification of the oil, the oleïn remains unchanged, whilst the solid fats are saponified. The mixture of soap and oleïn is treated with dilute alcohol, which dissolves the soap, while the oleïn collects as an oily layer upon the surface.

It has been already mentioned that the liquid portion of the oils has not the same composition throughout the different varieties of these substances: the oleïn of olive oil differs from the oleïn of linseed oil, or *linoleïn*; and both of these differ from the oleïn contained in castor oil.

(c) *Action of Bases upon Fatty Matters.—Soap-making.*

(1141) It is well known that however thoroughly water and oily matters may be incorporated by mixture, they do not unite to form a homogeneous compound; but that after a short time the grease separates and floats upon the surface. If, however, a quantity of a solution of caustic soda be added to the mixture, and it be then agitated, a milky-looking fluid or emulsion will be formed, and the oil will remain mixed with the water.

If a sufficient quantity of alkali be added, this emulsion when boiled for some hours gradually becomes clear; and a period arrives at which a transparent ropy fluid is formed, which froths strongly on agitation, and presents the characters of a concentrated solution of soap.

If to a portion of this clear liquid a strong solution of common salt be added, a curdling is immediately produced: the liquid separates into a clear solution which retains the glycerin, whilst a granular substance rises to the surface: this substance, if drained, pressed, and dried, exhibits the properties of soap.

Ordinary soap is freely soluble in hot water, forming with it a transparent solution, which, if tolerably strong, becomes a white opaque jelly as it cools; soap may also be dissolved by hot alcohol, which as it evaporates leaves the soap in transparent blocks. It is quite insoluble in strong brine, and in a concentrated solution of caustic potash or of soda; hence by the addition of chloride of sodium, or of caustic alkali, to a solution of soap, the soap is separated from the liquid in the solid form.

(1142) *Varieties of Soap.*—There are various kinds of soap, dependent on the nature of the fat, as well as upon that of the base used in its preparation. The base of the *hard soaps* is soda, that of the *soft soaps* is potash. The common soft soaps have always a more powerful alkaline reaction than the hard soaps, owing to the presence of an excess of alkali, which adds to their detergent power; they also usually contain the glycerin of the fat, which the manufacturer has not been at the pains to separate. If the oil be heated with oxide of lead, instead of with alkali, a white, solid, fusible compound, well known as *lead plaster*, is formed; which is, in fact, a soap containing oxide of lead as its base, instead of soda or potash. The earths if boiled with the oils also produce soaps; but such soaps are insoluble in water, and it is owing to the formation of these compounds that the *curdling* of soap by *hard* water is occasioned. Now, hard waters are waters which contain a certain quantity of earthy salts—usually of lime or of magnesia. When ordinary soap is dissolved in these waters double decomposition occurs, the lime displaces the alkali in the soap, and the alkali in turn combines with the acid which was previously united with the lime; and the insoluble lime soap thus formed, produces the curdling in question.

The soaps of the alkalies, or commercial soaps, are the only ones which are soluble in distilled water as well as in alcohol and in ether; but alcohol dissolves many of the compounds which the fatty acids form with the oxides of copper, iron, and manganese. Oil of turpentine and the fixed oils likewise dissolve small quantities of these soaps.

(1143) *Process of Soap-making.*—The unctuous materials which are used in this country in the preparation of hard soap are tallow, which gives the hardest soap, palm oil, and kitchen grease: rosin is also an ingredient in yellow soap. The coarse soft soaps are made of common fish oil and hemp-seed oil.

The manufacture of soap is carried on in large iron boilers called *coppers*, in which the mixture of ley and fat is heated by means either of an open fire, or of steam: the steam is either admitted into the copper by a perforated pipe, or it is made to circulate within it through a closed coil or worm. For hard soaps the leys of caustic soda are prepared in large iron vats, which are also heated by steam. Water is put into the vat and made to boil; a mixture of soda ash and slacked lime is then added in quantity sufficient to make the ley of the sp. gr. of 1·15; after boiling for some time the steam is turned off, the carbonate of lime allowed to subside, and the clear ley is drawn off. Fresh water is added to the residue, and thus a weaker ley is obtained.

Mottled soap is prepared from tallow, palm oil, and kitchen stuff. For every ton of tallow or fat introduced into the boiler, about 150 gallons of partly exhausted soda ley is added from a previous charge. When it first boils, a milky liquid is formed, which by degrees becomes more and more viscid; strong leys are then gradually added, and the boiling is continued until the soap ceases to feel greasy. A quantity of common salt is next added to separate the spent leys; these contain the glycerin and some impurities derived from the grease; they are drawn off from the bottom, and are thrown away. Strong ley is then added and the boiling continued, until the soap separates from the ley which retains an excess of alkali. It is then *cleansed* or transferred to the soap frames to cool. These frames are rectangular in shape, and consist of cast-iron plates cramped together by bolts and nuts; in these frames a small portion of the ley contained in the hot soap gradually separates, and accumulates in the lower part of the frame; this part of the soap is pared off, and is re-melted and added to the next charge. The soap remains in the frames for four or five days to cool and harden. At the end of that time it is cut up with wires into bars.

The *mottling* occurs in the moulds spontaneously, and is due to the separation from the mass of a small portion of iron soap, which gradually arranges itself in blue veins. This mottling is chiefly prized as a test that the soap is not too moist; since if too large a proportion of water were present, the colouring matter would sink to the lower part of the frame and accumulate there. Good soap contains about 30 per cent. of water; and 100 parts of fat or oil yield from 150 to 155 of such soap. A soda soap, before drying, contains about 6 or 7 per cent. of alkali.

Curd soap is usually obtained from tallow only, a small portion of olive oil or of lard being sometimes added. The soap while hot is put into a pan and *crutched,* or stirred forcibly, to break up the grain; it is then conveyed to the frames. When cold it should be perfectly smooth and white. *Yellow* soap is made from tallow and palm oil, and in addition to the alkali and fat, contains a considerable proportion of common rosin, which possesses acid properties and unites with the alkali: it is manufactured by a process similar to that used for mottled soap, but instead of being *cleansed,* or put into the frames immediately after boiling, it is *fitted,* or mixed in the copper, with a small quantity of water, which in two or three days carries down the excess of alkali, forming the *negur,* which subsides to the bottom; while a spongy crust, termed the *fob*, rises to the surface. The fob is skimmed off, and the semi-solid pasty mass of soap is transferred to the frames. The negur and fob are added to the next boil.

Marseilles and Castile soaps are made from olive oil and soda; they are mottled by the addition of green vitriol and sulphuretted lye to the soap while in the pasty state.

(*d*) *Manufacture of Fatty Acids for Candles.*

(1144) Large quantities of the fats are converted into the form of free acids, in the manufacture of what are often incorrectly termed stearin candles. This branch of industry has within the last few years acquired enormous magnitude. The fatty acids are prepared for this purpose by three principal methods;—in the first of these processes the fat is saponified by means of lime; in the second the fat or oil is decomposed by sulphuric acid; and in the third process the fat is separated into glycerin and the fatty acid, under the influence of water at an elevated temperature. The acids furnished by the fats are, at ordinary temperatures, whiter and harder than the fats from which they are obtained, and they are at the same time cleaner and more combustible.

1. *Saponification by Lime.*—Until recently it was the general practice to saponify the oils or fats by means of lime, which readily effects the desired change, and has the advantage of being much cheaper than either potash or soda: this process is still extensively followed in France. The tallow is melted by injecting hot steam into the vat which contains it, and milk of lime is added; the whole being maintained at the temperature of 212° by continually injecting steam through a perforated pipe, whilst the mixture is kept constantly stirred. An insoluble lime soap is thus formed; it is drained from the solution of glycerin, and then decomposed by the cautious addition of sulphuric acid diluted to the sp. gr. 1·160. The melted fatty acids thus rise in the form of an oil to the surface of the heated mixture; they are now decanted, and are washed, first with a fresh portion of heated dilute sulphuric acid, and afterwards with water. The fused acids are then cast into thin plates or cakes not much exceeding an inch in thickness; these cakes when cold are placed between layers of cocoa-nut matting, and are piled up one above another with iron plates interposed between every four or five cakes, and the pile thus formed is subjected to intense pressure by the aid of a powerful hydraulic press. By this means the oleic acid is in great measure forced out, whilst the harder palmitic and stearic acids

remain, and are afterwards subjected to pressure at a higher temperature; a fresh portion of the more fusible fat is removed by this operation, and the residue becomes beautifully white. In order to remove any traces of oxide of iron which the fat may have absorbed from the machinery, it is again washed, first with warm dilute sulphuric acid, then with water, and finally is melted and moulded into candles. The oleic acid furnishes with soda a soap sufficiently hard to be used for many purposes in the arts.

M. Milly has ascertained that the complete saponification of fats may be effected by a proportion of lime not exceeding 4 per cent. of the weight of the fat, by exposing the mixture, in a Papin's digester, with water to a high temperature. This temperature, according to Pelouze, need not be higher than from 311° to 329°. If water alone be employed, a temperature of not less than 428°, prolonged for many hours, is needed.

(1145) 2. *Acidification of the Fats by Sulphuric Acid.*—The action of sulphuric acid upon the fixed oils has been particularly examined by Fremy (*Ann. de Chimie,* II. lxv. 113). When concentrated sulphuric acid is made to act at ordinary temperatures upon an oil or fat, the fat at first combines with the acid, and the compound thus formed gradually becomes decomposed into sulphoglyceric (1148), sulpholeic, sulphopalmitic, and sulphostearic acids. The last three sulpho-acids are insoluble in acidulated water, but are dissolved by pure cold water. They have an oily bitter taste. On raising the temperature of the solution they become decomposed, the sulphuric acid is set at liberty, and the glycerin and the fatty acids are separated. The sulpholeic acid is more permanent than the sulpho-compounds of the solid fatty acids.

If the sulphuric acid and the oil or fat be made to act upon each other at a high temperature, the fat is immediately broken up into glycerin and the fatty acids, whilst the glycerin is in its turn decomposed, at the expense of a portion of the sulphuric acid, and sulphurous and carbonic acids are evolved. This reaction is employed on a large scale for the preparation of the so-called composite or stearin candles, and in England it has very nearly superseded the lime process.

The following is the method in which sulphuric acid is applied for this purpose by Messrs. Wilson at the works of Price's Patent Candle Company:—The fat is first melted and freed from impurities, then mixed with from one-sixth to one-seventh of its weight of oil of vitriol in large copper boilers, where it is raised by means of a current of highly heated steam to a temperature of about 350°. This temperature is maintained for about two hours, the mass being frequently stirred briskly; during this process carbonic and sulphurous acids are disengaged in large quantities, nearly all the glycerin and sulphuric acid being decomposed in the course of the operation. The liberated fatty acids are of a dark colour, and require thorough washing with water to free them from adhering sulphuric acid.

The impure fatty acids thus obtained are then subjected to distillation, which is effected by placing them in a copper vessel, into the lower part of which a current of steam at the ordinary pressure is injected; previous to its admission to the still this steam is heated to about 600°, by transmitting it through pipes heated nearly to redness. The distillation does not take place below 400° F., but towards the latter part of the process the temperature frequently rises to 500°. After the acidified fats have been distilled as far as is advantageous, the dark residue in the retort may still be made to yield a considerable amount of fat by submitting it to pressure; the black solid mass which still remains is used as fuel. The distilled fat is broken up into fragments, and distributed in layers of about three-fourths of an inch in thickness upon squares of cocoa-nut matting, which are piled one above another, and submitted to the action of the hydraulic press. The fat thus obtained is sufficiently firm to be made at once into candles suited to European climates, but for the Indian market it is necessary again to subject the fat to pressure, which this time is effected at a temperature of 120°.

(1146) 3. *Action of Water at a high temperature on Fats and Oils.*—Mr. Tilghmann a few years ago made the important observation, that when a mixture of fat and water is forced under strong pressure through tubes heated nearly to redness, so as to raise the temperature of the mass to 400° or 500°, the fat is entirely decomposed into glycerin and fatty acids; the elements of water enter into combination with those of the fat, and by this means a result is obtained exactly the reverse of that effected by Berthelot at lower temperatures (1149), when the acid and glycerin are digested together.

Mr. Wilson by injecting superheated steam at a temperature of between 500° and 600° into heated fat, was able to produce a similar separation of hydrated glycerin and of the acids with which it was previously in combination; and at the same time he succeeded in effecting the distillation, not only of the fat, but also of the glycerin; the latter is thus obtained in a high degree of concentration, as a beautiful, colourless, syrupy liquid, which can be prepared in almost unlimited quantity. The fatty acids are also procured by the same operation in a very pure form, so that this process, from its simplicity, and from the purity of the products which it yields, bids fair to supersede those previously employed in the preparation of the fatty acids for illuminating purposes. The operation, however, cannot be conducted so rapidly as the process of decomposition by sulphuric acid.

§ II. GLYCERIN.—THE GLYCERIDES.

(1147) GLYCERIN ($C_6H_8O_6$), *the sweet principle of oils.*—This substance is separated from all fatty and oily bodies (with the exception of spermaceti and the different varieties of wax), during the process of saponification by alkalies. It is a viscid, colourless liquid of a sweet taste, and of the sp. gr. 1·28, at 59°. It is soluble in water and alcohol in all proportions, but is sparingly soluble in ether. Glycerin dissolves most of the deliquescent salts, as well as many other substances which are soluble in water. Baryta, lime, and strontia, are freely soluble in glycerin, and the solutions are not precipitated by carbonic acid. Glycerin is slightly volatile at 212°, but, if distilled alone, the greater part of it experiences decomposition; intensely pungent vapours of acrolein ($C_6H_4O_2$; 1151) are then disengaged, which excite a most painful irritation of the eyes. When heated sufficiently in air, glycerin burns with a luminous flame. It may, however, be distilled without alteration, in a current of superheated steam which has been raised to a temperature of between 500° and 600°; advantage is taken of this fact in order to prepare glycerin in large quantities (1146). The usual method of obtaining glycerin on a small scale consists in saponifying olive oil by heating it with an equal weight of litharge: the oxide of lead is mixed with water and added to the oil, with which it is boiled till the saponification is complete; fresh portions of water being added from time to time to supply the place of that which is evaporated. The glycerin is dissolved by the water, and is easily freed from the insoluble *lead plaster*, or mixed oleate and margarate of lead which is formed. The aqueous solution retains a small quantity of oxide of lead, which may be separated by transmitting through it a current of sulphuretted hydrogen, and filtering from the precipitated sulphide of lead; the water may then be expelled by evaporation *in vacuo* at a temperature not exceeding 300° F. If the solution be evaporated in the open air, it becomes brown.

When glycerin is heated with hydrate of potash, it is decomposed into a mixture of acetate and formiate of potash, whilst hydrogen escapes :—

$$\overbrace{C_6H_8O_6}^{\text{Glycerin.}} + 2\,(HO,\ KO) = \overbrace{KO, C_4H_3O_3}^{\text{Acetate of Potash.}} + \overbrace{KO, C_2HO_3}^{\text{Formiate of Potash.}} + 2\,HO + 4\,H.$$

Glycerin is not susceptible of the vinous fermentation; but according to Redtenbacher (Liebig's *Annal.* lvii. 174), if a dilute solution of glycerin be mixed with well-washed yeast, and kept for some weeks at a temperature of from 70° to 85°, water being added as it evaporates, it becomes slowly converted into propionic acid; very little evolution of gas occurs, but the liquid becomes mouldy and acquires an acid reaction: if the mixture be neutralized from time to time with carbonate of soda, and as soon as the further development of acid ceases, the liquid be filtered and evaporated, a yellow saline mass is obtained, possessing the smell of *sauer-kraut:* when this saline mass is distilled after the addition of sulphuric acid, propionic acid is the principal product condensed in the receiver. The connexion between the composition of propionic acid and glycerin is very simple, hydrated propionic acid with two equivalents of water containing the elements of glycerin :—

$$\overbrace{C_6H_8O_6}^{\text{Glycerin.}} = \overbrace{HO, C_6H_5O_3}^{\text{Propionic Acid.}} + 2\,HO.$$

Glycerin admits of oxidation without difficulty; if distilled with dilute sulphuric acid and oxide of manganese, formic acid is amongst the products; and under the combined influence of platinum black and atmospheric air it rapidly absorbs oxygen and yields an acid, the nature of which has not been ascertained. The class of compounds to which glycerin should be referred, is not as yet fully made out, but it is probably a teratomic alcohol (1149).

An interesting series of experiments was made by Berthelot and De Luca, upon the action of biniodide of phosphorus upon glycerin (*Ann. de Chimie,* III. xliii. 257). When equal parts of crystallized iodide of phosphorus (PI_2) and of glycerin are mixed in a capacious retort, considerable heat is developed; a new compound (C_6H_5I) mixed with water distils over: it is called *iodized propylene,* but the name *iodide of allyl* would be more appropriate (1246); a considerable volume of pure gaseous tritylene (propylene) is also evolved,* whilst free iodine and phosphorous acid remain in the retort, mixed with the excess of glycerin employed. The reaction is a remarkable one, for it will be observed that the whole of the oxygen of the glycerin is removed, one portion of it uniting with the phosphorus to form phosphorous acid, and the remaining portion being eliminated with hydrogen in the form of water, whilst the carbon remains in the form of iodide of allyl :—

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* Pure tritylene is readily obtained for laboratory use by distilling 1 part of iodide of allyl with 5 parts of mercury and 2 of concentrated hydrochloric acid. An ounce of iodide of allyl thus yields more than 150 cubic inches of the gas; $C_6H_5I + HCl + 4\,Hg = C_6H_6 + Hg_2I + Hg_2Cl$. Tritylene remains gaseous at —40°, but it may be liquefied under pressure. Its odour resembles that of olefiant gas. Essence of turpentine, ether, chloroform, and benzole each dissolves from 13 to 18 times its volume of this gas.

$$\overbrace{PI_2}^{\text{Iodide of Phosphorus.}} + \overbrace{C_6H_8O_6}^{\text{Glycerin.}} = \overbrace{C_6H_5I}^{\text{Iodide of Allyl.}} + \overbrace{2\,HO, PO_3}^{\text{Phosphorous Acid.}} + HO + I.$$

The tritylene which is disengaged is the result of a secondary action, connected probably with the formation of a peculiar iodized compound (? iodhydrin $C_{12}H_{11}IO_6$) which is found in the retort in small quantity.

(1148) *Action of Acids upon Glycerin.*—Nitric acid rapidly attacks glycerin, and converts it into carbonic and oxalic acids. If glycerin be allowed to fall drop by drop into a mixture of equal measures of nitric acid and oil of vitriol, care being taken to prevent the temperature from rising too high, a heavy oily-looking liquid collects at the bottom of the acid. It is powerfully explosive, and detonates either by a blow or by elevation of temperature; a single drop placed upon paper and struck upon an anvil, producing a deafening report. This body is a substitution compound of glycerin, in which 2 equivalents of hydrogen are displaced by an equal number of equivalents of peroxide of nitrogen. It has been termed *nitro-glycerin* ($C_6H_6(NO_4)_2O_6$; De Vrij). It is insoluble in alcohol and in ether; it has a sweetish, pungent, aromatic taste, and if but a single drop be placed upon the tongue, it produces a painful aching in the back of the head, which lasts for many hours.

Glycerin enters like alcohol into combination with many of the polybasic acids, forming compounds analogous to sulphethylic acid. Thus, when oil of vitriol is mixed with half its weight of glycerin, the two bodies unite with considerable evolution of heat: the compound acid forms soluble salts with lime and baryta; the lime salt, according to Pelouze, has the formula ($CaO, C_6H_7O_5, 2\,SO_3$), the sulpho-glyceric acid saturating only half the quantity of base which would be required by the sulphuric acid which it contains. A compound similar to those above described may be formed with glycerin and phosphoric acid; it is very soluble both in water and in alcohol, but is easily decomposed into free phosphoric acid and glycerin. Phosphoglyceric acid exists ready formed in the yolk of the egg (Gobley), and probably also in the brain.

(1149) *Artificial Formation of Fats.—Glycerides.*—The most important compounds which result from the action of acids upon glycerin are those termed *glycerides*, which are analogous in composition to the various fats and oils. Berthelot has recently succeeded in forming these bodies by the direct union of the acids with glycerin, and has obtained in the course of his investigation, not only a large class of these bodies which were not previously known, but has been successful in the attempt to recombine glycerin with the fatty acids, so as to re-produce several of the natural fats (*Ann. de Chimie*, III. xli. 216.) According to the researches of this chemist, stearic, palmitic, and oleic acids each forms three compounds by its union with glycerin; the act of combination is, however, attended by the separation of water in each case; but there is some difficulty in explaining why in the compounds which are formed from two equivalents of acid, the quantity of water which is separated should be exactly that stated by Berthelot; and the analysis of the simpler compounds with acetic acid, which are formed by a series of changes analogous to that by which the more complex fats are formed, appears to leave some doubt of his accuracy on this point. The following table contains a list of these compounds with the formulæ of the decomposition which appears to attend their formation. For the sake of convenience the formulæ of the hydrated acids are written without indicating the basic water in the usual manner; thus, stearic acid ($HO, C_{36}H_{35}O_3$) is written ($C_{36}H_{36}O_4$) :—

			Stearic Acid.		Glycerin.	
Monostearin	= $C_{42}H_{42}O_8$	=	$C_{36}H_{36}O_4$	+	$C_6H_8O_6$	− 2 HO
Bistearin	= $C_{78}H_{78}O_{12}$	=	2 ($C_{36}H_{36}O_4$)	+	$C_6H_8O_6$	− 2 HO?
Terstearin	= $C_{114}H_{110}O_{12}$	=	3 ($C_{36}H_{36}O_4$)	+	$C_6H_8O_6$	− 6 HO
			Palmitic Acid.			
Monopalmitin	= $C_{38}H_{38}O_8$	=	$C_{32}H_{32}O_4$	+	$C_6H_8O_6$	− 2 HO
Bipalmitin	= $C_{70}H_{70}O_{12}$	=	2 ($C_{32}H_{32}O_4$)	+	$C_6H_8O_6$	− 2 HO?
Terpalmitin	= $C_{102}H_{98}O_{12}$	=	3 ($C_{32}H_{32}O_4$)	+	$C_6H_8O_6$	− 6 HO
			Oleic Acid.			
Monolein	= $C_{42}H_{40}O_8$	=	$C_{36}H_{34}O_4$	+	$C_6H_8O_6$	− 2 HO
Biolein	= $C_{78}H_{74}O_{12}$	=	2 ($C_{36}H_{34}O_4$)	+	$C_6H_8O_6$	− 2 HO?
Terolein	= $C_{114}H_{104}O_{12}$	=	3 ($C_{36}H_{34}O_4$)	+	$C_6H_8O_6$	− 6 HO
			Valeric Acid.			
Monovalerin	= $C_{16}H_{16}O_8$	=	$C_{10}H_{10}O_4$	+	$C_6H_8O_6$	− 2 HO
Bivalerin	= $C_{26}H_{26}O_{12}$	=	2 ($C_{10}H_{10}O_4$)	+	$C_6H_8O_6$	− 2 HO?
Tervalerin	= $C_{36}H_{32}O_{12}$	=	3 ($C_{10}H_{10}O_4$)	+	$C_6H_8O_6$	− 6 HO
			Butyric Acid.			
Monobutyrin	= $C_{14}H_{14}O_8$	=	$C_8H_8O_4$	+	$C_6H_8O_6$	− 2 HO
Bibutyrin	= $C_{22}H_{22}O_{12}$	=	2 ($C_8H_8O_4$)	+	$C_6H_8O_6$	− 2 HO?
Terbutyrin	= $C_{30}H_{26}O_{12}$	=	3 ($C_8H_8O_4$)	+	$C_6H_8O_6$	− 6 HO

$$\begin{aligned}
&\text{Monoacetin} &&= C_{10}H_{10}O_8 = \overbrace{C_4H_4O_4}^{\text{Acetic Acid.}} + \overbrace{C_6H_8O_6}^{\text{Glycerin.}} - 2\,HO\\
&\text{Biacetin} &&= C_{14}H_{12}O_{10} = 2\,(C_4H_4O_4) + C_6H_8O_6 - 4\,HO\\
&\text{Teracetin} &&= C_{18}H_{14}O_{12} = 3\,(C_4H_4O_4) + C_6H_8O_6 - 6\,HO\\
&\text{Monobenzoicin} &&= C_{20}H_{12}O_8 = \overbrace{(C_{14}H_6O_4)}^{\text{Benzoic Acid.}} + C_6H_8O_6 - 2\,HO\\
&\text{Terbenzoicin} &&= C_{48}H_{20}O_{12} = 3\,(C_{14}H_6O_4) + C_6H_8O_6 - 6\,HO\\
&\text{Sebacin} &&= C_{32}H_{30}O_{16} = \overbrace{C_{20}H_{18}O_8}^{\text{Sebacic Acid.}} + 2\,(C_6H_8O_6) - 4\,HO\\
&\text{Monochlorhydrin} &&= C_6H_7ClO_4 = HCl + C_6H_8O_6 - 2\,HO\\
&\text{Bichlorhydrin} &&= C_6H_6Cl_2O_2 = 2\,HCl + C_6H_8O_6 - 4\,HO\\
&\text{Epichlorhydrin} &&= C_6H_5ClO_2 = HCl + C_6H_8O_6 - 4\,HO\\
&\text{Benzochlorhydrin} &&= C_{20}H_{11}ClO_6 = \overbrace{C_{14}H_6O_4}^{\text{Benzoic Acid.}} + HCl + C_6H_8O_6 - 4\,HO\\
&\text{Biethylin} &&= C_{14}H_{16}O_6 = 2\,\overbrace{(C_4H_6O_2)}^{\text{Alcohol.}} + C_6H_8O_6 - 4\,HO.
\end{aligned}$$

It might have been expected that in the formation of these compounds the quantity of water separated should have been somewhat different, and that the proportions in each of the three compounds should have been 2 HO in the first, 4 HO in the second, and 6 HO in the third, each equivalent of the hydrated acid losing an equivalent of water, whilst the single equivalent of glycerin, in the act of combination, should lose 1, 2, and 3 equivalents of water, according to the number of equivalents of acid with which it is combined (see *note*, p. 383).

According to Berthelot, terstearin, terpalmitin, and terolein, are identical with the stearin, palmitin, and olein of the natural fats, and they are produced by the combination of 3 equivalents of the hydrated fatty acids ($C_nH_nO_4$) with 1 equivalent of glycerin, the act of combination being attended with the separation of 6 equivalents of water. These combinations of glycerin with the acids may be obtained either by heating the acid and the glycerin together for several hours in closed vessels at an elevated temperature; or by mixing the glycerin and fatty acid with hydrochloric, sulphuric, phosphoric, or tartaric acid, and exposing the mixture for many hours to a temperature of 212°. A partial formation of these bodies occurs even without the aid of the stronger acids if the glycerin and the fatty acid be kept in contact for several months at the ordinary temperature.

All these neutral compounds of the fatty acids with glycerin are insoluble in water, but are soluble to some extent in boiling alcohol, and are readily soluble in ether. If treated with concentrated acids they are decomposed and acidified in the same manner as the natural fats; and they are all saponifiable,—that is, they are decomposed like the natural fats, into a fatty acid and glycerin, when boiled with an alkali. It has been found that whether monacid, biacid, or teracid in composition, these fats are all neutral in their reactions, and moreover when decomposed, they all yield glycerin of the same composition and condition of hydration. This observation is important as it diminishes the probability of the view of Berzelius regarding the nature of glycerin. It is obvious that the formula usually given for glycerin ($C_6H_8O_6$) does not represent the substance which, when in combination with the acid, produces the oil. Berzelius considered that the body which was present in the oil consisted of C_3H_2O, and he gave it the name of *oxide of lipyl.* This substance has not been isolated; but it was supposed that at the moment of its liberation it combined with 2 equivalents of water and became converted into glycerin:—

$$\overbrace{2\ (C_3H_2O)}^{\text{Oxide of Lipyl.}} \quad + \quad 4\ HO \quad = \quad \overbrace{C_6H_8O_6}^{\text{Glycerin.}}.$$

Liebig proposed to consider glycerin as an alcohol: if it be an alcohol, it is not improbable that it is a *teratomic* one, since the natural fats all appear to be compounds derived from one equivalent of glycerin and three equivalents of the fatty acid. The results of the decomposition of bichlorhydrin and of iodhydrin, which will be alluded to presently, also tend to strengthen this view.

Monostearin has the aspect of bees' wax; it fuses at 141°·8, and solidifies at 140°. It is prepared by heating equal parts of stearic acid and glycerin to 392° for a couple of days in a sealed tube: the substance thus formed is freed from excess of stearic acid by digestion with slaked lime at a temperature of 212° for a quarter of an hour. The lime combines with the excess of stearic acid, but does not decompose the monostearin, which is afterwards separated from the lime soap by digesting the mixture in hot ether, from which the stearin crystallizes in stellate doubly refracting needles. *Bistearin* may be prepared by heating to 212° for six days, equal parts of glycerin and stearic acid; it resembles the first compound in appearance, crystallizing in oblique doubly refracting plates, which fuse at 136°·4, and become solid at 131°. *Terstearin,* which Berthelot considers identical with natural stearin, may be obtained by digesting monostearin for three hours at a temperature of 518° with fifteen or twenty times its weight of stearic acid: it is purified from the excess of stearic acid by lime and ether, as directed for monostearin. Valeric, butyric, and acetic acids have each, in like manner, been combined with glycerin in three proportions, but no compound could be obtained with formic acid. It is interesting to remark that even the compounds with acetic acid present the appearance of oily bodies, and are very sparingly soluble in water. It is not unlikely that acetin is one of the components of cod-liver oil, since acetic acid is found amongst the products of the saponification of this oil.

(1150) Glycerin has also been similarly combined with other organic acids, such as the benzoic and the camphoric; as well as with hydrochloric, hydrobromic, and hydriodic acids.

Chlorhydrin ($C_6H_7ClO_4$) is obtained by saturating glycerin with hydrochloric acid gas, and maintaining the mixture at 212° for thirty-six hours: it is to be neutralized with carbonate of potash, and agitated with ether; the ethereal solution when evaporated leaves chlorhydrin as a neutral oil, with a cooling ethereal odour, and a sweetish, pungent taste. It is soluble in water and in ether: it boils at 440°, and may be distilled unchanged.

Bichlorhydrin ($C_6H_6Cl_2O_2$) *Sp. gr.* 1·37.—This is a neutral oil which has a well-marked ethereal odour. It boils at 352°, and remains liquid at —30°. It burns with a white flame, bordered with green.

Epichlorhydrin ($C_6H_5O_2Cl$); *sp. gr.* between 1·2 and 1·3. —This substance is a limpid oil which boils between 248° and 266°, emitting a vapour of an ethereal odour resembling that of hydrochloric ether. It is prepared by heating bichlorhydrin for several hours in a sealed tube to 212°, with 12 or 15 parts of fuming hydrochloric acid; after which it is neutralized with lime and distilled. The mode in which these chlorinated compounds are formed is indicated in the Table at page 380.

Iodhydrin ($C_{12}H_{11}IO_6$?) *Sp. gr.* 1·783.—When glycerin is saturated with hydriodic acid gas, and heated to 212° for forty hours, then treated with potash and with ether, it yields a golden yellow syrupy liquid, which dissolves one-fifth of its bulk of water, but is not itself soluble in water. The formation of this body is rather anomalous:—

$$\overbrace{2\ (C_6H_8O_6)}^{\text{Glycerin.}} \quad + \quad HI \quad = \quad \overbrace{C_{12}H_{11}IO_6}^{\text{Iodhydrin.}} \quad + \quad 6\ HO.$$

Iodhydrin has a sweet taste; it is combustible, and cannot be distilled without experiencing decomposition. When treated with an aqueous solution of potash it is slowly decomposed; iodide of potassium and glycerin are formed, together with a volatile compound, which is soluble in ether, and which has a composition represented by $C_6H_5O_3$. This substance would correspond to the ether of glycerin, admitting glycerin to be a kind of alcohol.

This supposed *glyceric ether** contains the elements of glycerin, minus 3 equivalents of water :—

$$\overbrace{C_6H_8O_6}^{\text{Glycerin.}} = \overbrace{C_6H_5O_3}^{\text{Glyceric Ether.}} + 3\,HO;$$

and its formation from iodhydrin might be thus represented :—

$$\overbrace{C_{12}H_{11}IO_6}^{\text{Iodhydrin.}} + KO,HO + HO = \overbrace{C_6H_8O_6}^{\text{Glycerin.}} + \overbrace{C_6H_5O_3}^{\text{Glyceric Ether.}} + KI.$$

Glycerin forms with hydrobromic acid several compounds analogous to those which it yields with hydrochloric acid. When an alcoholic solution of bibromhydrin ($C_6H_6Br_2O_3$) is submitted to the action of gaseous ammonia, the hydrobromate of a new base, *glyceramine*, $C_6H_9NO_4$ (Berthelot and De Luca), is produced, whilst bromide of ammonium is formed. The correctness of the formula given for this base is however questionable.

Biethylin ($C_{14}H_{16}O_6$), *sp. gr.* 0·92, is a limpid oil of a pungent, ethereal odour; it boils at 376°, and does not become solid at —40°; it is scarcely soluble in water. This singular compound is obtained by acting upon a mixture of bromide of ethyl, glycerin, and hydrate of potash; the materials are enclosed in a sealed tube, and submitted for four days to a temperature of 212° :—

$$\overbrace{2\,(C_4H_5Br)}^{\text{Bromide of Ethyl.}} + \overbrace{C_6H_8O_6}^{\text{Glycerin.}} + 2(KO,HO) = \overbrace{C_{14}H_{16}O_6}^{\text{Biethylin.}} + 2\,KBr + 4HO.$$

or it may be regarded as the result of the combination of two

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* Glycerin, however, if it be an alcohol, cannot be a monatomic alcohol, but it must be teratomic; in which case it may be formed as Gerhardt suggests, upon the type of two double molecules of water, and its radicle ($C_6H_5O_2$) may be named *glycyl*, in order to distinguish it from Liebig's *glyceryl* (C_6H_7). The relation of the three acetins to glycerin would then be the following :—

$$\overbrace{\left.\begin{matrix}C_6H_5O_2\\H\end{matrix}\right\}O_2,\ \left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Glycerin.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_6H_5O_2\\C_4H_3O_2\end{matrix}\right\}O_2,\ \left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Acetin.}};$$

$$\overbrace{\left.\begin{matrix}C_6H_5O_2\\H\end{matrix}\right\}O_2,\ \left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}O_2}^{\text{Biacetin.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_6H_5O_2\\C_4H_3O_2\end{matrix}\right\}O_2,\ \left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}O_2}^{\text{Teracetin.}}.$$

Wurtz, however, considers glycerin to be formed upon the type of three double molecules of water, $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_6$; a view which is more consistent with the general theory of these compounds (1185); C_6H_5 being a teratomic radicle, or representing three equivalents of hydrogen; thus :—

$$\overbrace{\left.\begin{matrix}(C_6H_5)\\H_3\end{matrix}\right\}O_6}^{\text{Glycerin.}};\ \overbrace{\left.\begin{matrix}(C_6H_5)\\(C_6H_5)\end{matrix}\right\}O_6}^{\text{Glyceric Ether.}};\ \overbrace{\left.\begin{matrix}(C_6H_5)\\C_4H_3O_2\\H_2\end{matrix}\right\}O_6}^{\text{Acetin.}};\ \overbrace{\left.\begin{matrix}(C_6H_5)\\2(C_4H_3O_2)\\H\end{matrix}\right\}O_6}^{\text{Biacetin.}};\ \overbrace{\left.\begin{matrix}(C_6H_5)\\3(C_4H_3O_2)\end{matrix}\right\}O_6}^{\text{Teracetin.}}.$$

equivalents of alcohol and one of glycerin, attended with the separation of four equivalents of water.

(1150 *bis*) *Compounds of Mannite with the Acids, analogous to Fats.*—Since the paragraph on mannite (935) was printed, an interesting paper has been published on this substance, by Berthelot (*Ann. de Chimie*, III. xlvii. 297). He finds that when mannite is heated to 400° in an open vessel and kept constantly stirred, it loses water, and becomes partially converted into a viscous substance which has a feebly sweet taste; it has been termed *mannitane.* This body contains the elements of 1 equivalent of mannite minus 1 equivalent of water:—

$$\overbrace{C_6H_7O_6}^{\text{Mannite.}} \quad = \quad \overbrace{C_6H_6O_5}^{\text{Mannitane.}} \quad + \quad HO.$$

Mannitane is deliquescent, and when exposed to the air it absorbs water slowly, and is reconverted into mannite. Mannitane appears to present a very close analogy with glycerin, as will be rendered apparent by the following details. When mannite is heated for some hours with the hydrated acids in sealed tubes under pressure, it gives rise to a series of compounds which run exactly parallel with those obtained by treating glycerin in a similar manner. If stearic acid be thus heated with mannite it forms two compounds, viz., *bistearo-mannite* and *terstearo-mannite*, which may be represented as formed thus:—

$$\overbrace{C_6H_7O_6}^{\text{Mannite.}} \quad + \quad \overbrace{2\,(C_{36}H_{36}O_4)}^{\text{Stearic Acid.}} \quad = \quad \overbrace{C_{78}\,H_{76}\,O_{11}}^{\text{Bistearo-mannite.}} \quad + \quad 3\ HO;$$

$$C_6H_7O_6 \quad + \quad 3\,(C_{36}H_{36}O_4) \quad = \quad \overbrace{C_{114}H_{108}O_{11}}^{\text{Terstearo-mannite.}} \quad + \quad 7\ HO.$$

These substances can scarcely be distinguished from bistearin and terstearin, which are the corresponding compounds of glycerin: they are solid crystalline fats, of about the same degree of fusibility as the stearins. They admit of being saponified in the same manner as the true fats; and when decomposed by bases they yield stearic acid, and a solution from which the sweet syrupy compound, mannitane, is obtained. This solution so greatly resembles that of glycerin in appearance and properties, that Berthelot thinks it is by no means improbable that some of the natural fats which are at present supposed to be compounds of glycerin, may turn out to be derivatives of mannite. Compounds of mannite similar to those which it forms with stearic acid, have been obtained by heating it with palmitic, butyric, acetic, benzoic, and other acids. Its compound with acetic acid, *aceto-mannite* ($C_{10}H_8O_7 = C_6H_7O_6 + C_4H_4O_4 - 3\ HO$) is a viscid, intensely bitter liquid, which emits, when warmed, a peculiar odour like that possessed by many of the umbelliferous plants. With hydrochloric acid, mannite yields a white, neutral, well-crystallized body ($C_6H_5ClO_3$), which has a bitter aromatic taste: it is very soluble in ether; and may be volatilized without residue. The fat-like derivatives of mannite are neutral bodies. Those which are produced from one equivalent of acid may be supposed to be formed by the union of 1 equivalent of *mannitane* and 1 equivalent of the normal hydrate of the acid, attended with the separation of 2 equivalents of water; whilst those containing 3 equivalents of acid are formed from one of mannitane and three of the normal acid, with the separation of 6 equivalents of water. But mannite also forms compounds with the polybasic acids, such as the sulphuric, the tartaric, and the phosphoric acids; these compounds have an acid character, and are analogous to the sulphoglyceric and phosphoglyceric acids (1148). Their formation is also attended with the elimination of water.

Saccharine bodies admit of subdivision into two classes; 1. True sugars, or those which are fermentable and contain an equal number of equivalents of oxygen and hydrogen; and 2. Those which are not fermentable and contain an excess of hydrogen over the oxygen. Berthelot states that the bodies which belong to the latter class, such as dulcose, quercite, and pinite (Table p. 71), possess the property, like mannite and glycerin, of entering into combination with the different acids, and forming compounds more or less analogous to those above described.

(1151) *Acrolein*, or *Acrylic Aldehyd* ($C_6H_4O_2 = C_6H_3O_2, H$); *Sp. gr. of vapour* 1·897.—When glycerin or any of its compounds is submitted to the ordinary process of distillation, it undergoes decomposition; and amongst the products is a substance which, from its intensely irritating effects upon the mucous membrane of the eyes and organs of respiration, has received the name of *acrolein*. This substance is best obtained in a state of purity (Redtenbacher, Liebig's *Ann.* xlvii. 114), by distilling in a capacious retort, a mixture of glycerin with anhydrous phosphoric acid, or with bisulphate of potash: the vapours must be condensed in a properly cooled receiver, which is luted on to the retort, and provided with a tube opening into a chimney with a good draught.

The object of using anhydrous phosphoric acid in the distillation is to effect the dehydration of the glycerin, since glycerin contains the elements of acrolein, and 4 equivalents of water:—

$$\overbrace{C_6H_8O_6}^{\text{Glycerin.}} = \overbrace{C_6H_4O_2}^{\text{Acrolein.}} + 4\,HO.$$

The distilled liquid separates into two layers, the upper one consisting of acrolein, and the lower one of an aqueous solution of the same substance, mixed with a quantity of acrylic acid. This distillate must be digested with finely powdered litharge in order to combine with the acid, and rectified by the heat of a water bath: the acrolein thus obtained must be submitted to a second rectification from chloride of calcium, after which it is nearly free from impurity. All these operations must be carried on in vessels filled with carbonic acid, for the purpose of excluding atmospheric oxygen, because acrolein becomes rapidly oxidized when exposed to the air.

Acrolein is a limpid, transparent, colourless liquid, lighter than water, and possessed of a high refracting power. It has a burning taste, and emits a vapour which is intolerably irritating: the boiling point of the liquid is about 125°. It burns with a clear luminous flame. Acrolein when pure is neutral to test paper; but, like ordinary aldehyd, it rapidly becomes acid by the absorption of oxygen from the air; a mixture of acrylic, acetic, and formic acids being produced. It is freely soluble in ether, but requires 40 parts of water for solution. Acrolein cannot long be preserved without change, even in sealed tubes; but becomes converted into a white, flocculent, and probably isomeric substance, termed *disacryl*, which is insoluble in water, acids, alkalies, oils, and bisulphide of carbon. Sometimes the acrolein becomes transformed into a resinoid body, which melts at 212°, and forms a brittle, transparent mass on cooling: this substance, though insoluble in water, is soluble in alcohol, in ether, and in alkaline solutions.

The reactions of acrolein with the alkalies, further show its similarity to aldehyd:—when mixed with a solution of potash or of soda it is rapidly acted upon; its irritating odour disappears and is succeeded by one of cinnamon, whilst a brown resinous substance is formed. The ethereal solution of acrolein when mixed with ammonia yields a white amorphous body, destitute of odour. When mixed with nitrate of silver it gives a white curdy precipitate, which is reduced to metallic silver on boiling, though without coating the glass with the reduced metal: acrylate of silver remains in solution. Oxide of silver rapidly oxidizes acrolein, with great evolution of heat, and converts it into acrylic acid (1175); the acid is indeed easily prepared by this means from the crude liquid obtained by the destructive distillation of the oils.

Hofmann and Cahours have succeeded in discovering the *allylic* (or, as they have less appropriately termed it, *acrylic*) *alcohol* (C_6H_5O, HO), a compound which stands in the same relation to acrolein that ethylic alcohol does to ordinary aldehyd; the same chemists have also prepared a large number of the derivatives of this alcohol, many of which have been long known as compounds of *allyl* (C_6H_5).

§ III. THE FATTY ACIDS.

(1152) THE FATS and fixed oils when saponified yield a number of acids, which belong to two different homologous series. Stearic and palmitic acids may be taken as the types of one series, in which the general formula of the normal acids is $(C_nH_n)O_4$. The general formula of the other series is $(C_nH_{n-2})O_4$; this series is represented by oleic acid, but only a few terms of it are known. By the oxidation of the members of these two groups a third series of acids may be obtained, to which suberic and succinic acid belong: the acids of this group are dibasic: their normal hydrates have the general formula $(C_nH_{n-2})O_8$. In the following table the corresponding acids in each of these three groups are enumerated:—

Acids of the form $(C_nH_n)O_4$, or $HO, C_nH_{n-1}O_3$.		Acids of the form $(C_nH_{n-2})O_4$, or $HO, C_nH_{n-3}O_3$.		Acids of the form $C_nH_{n-2}O_8$, or $2\,HO, C_nH_{n-4}O_6$.	
Melissic	. $C_{60}H_{60}O_4$				
Cerotic .	. $C_{54}H_{54}O_4$				
Arachidic	. $C_{40}H_{40}O_4$				
Stearic .	. $C_{36}H_{36}O_4$	Oleic .	. $C_{36}H_{34}O_4$		
Palmitic	. $C_{32}H_{32}O_4$	Physetoleic	$C_{32}H_{30}O_4$		
Myristic	. $C_{28}H_{28}O_4$				
Lauric .	. $C_{24}H_{24}O_4$				
Rutic .	. $C_{20}H_{20}O_4$			Sebacic .	. $C_{20}H_{16}O_8$
Pelargonic	. $C_{18}H_{18}O_4$				
Caprylic	. $C_{16}H_{16}O_4$			Suberic .	. $C_{16}H_{12}O_8$
Œnanthylic	$C_{14}H_{14}O_4$			Pimelic .	. $C_{14}H_{10}O_8$
Caproic .	. $C_{12}H_{12}O_4$			Adipic .	. $C_{12}H_8O_8$
Valeric .	. $C_{10}H_{10}O_4$	Angelic .	. $C_{10}H_8O_4$	Lipic ? .	. $C_{10}H_6O_8$
Butyric .	. $C_8H_8O_4$			Succinic	. $C_8H_4O_8$
Propionic	. $C_6H_6O_4$	Acrylic .	. $C_6H_4O_4$		
Acetic .	. $C_4H_4O_4$			Oxalic .	. $C_4H_2O_8$
Formic .	. $C_2H_2O_4$				

(*a*) *Acids belonging to the Stearic Series* ($HO, C_nH_{n-1}O_3$).

(1153) The acids which are comprised in this series constitute one of the most numerous and most carefully examined groups of homologous compounds; all the terms of which, commencing with the formic and proceeding as far as the rutic, are well known. The number of equivalents of carbon in each of these terms is divisible by 2. It has been remarked, that in the terms which contain more carbon than the rutic, the number of equivalents of carbon in all the acids which have been satisfactorily examined, is divisible by 4; although many chemists admit the existence of acids corresponding in composition to all the hydrocarbons divisible by 2, up to ($C_{40}H_{40}$). The fusing point of Brodie's cerotic acid is so much lower than that which might have been expected from an acid so high in the series, that Heintz has suggested that this exceptional case may probably arise from the acid being a mixture of two others; since he finds it to be a general rule, that a mixture of any two of the solid acids of this series has a fusing point considerably below that of either of its components (1156).

The acids belonging to this group may all be distilled, either partially or completely, without undergoing decomposition. Many of them exhibit a remarkable peculiarity in the volume of vapour which they furnish at different temperatures; thus, the formic, the acetic, the butyric, and the valeric acids, at low temperatures, furnish a much smaller volume of vapour than they do at more elevated temperatures:—

	° F.	Vapour density.
Formic acid at . .	51	3·23
Ditto, ditto . .	416	1·61
Acetic acid at . .	69	3·95
Ditto, ditto . .	320	2·48
Ditto, ditto . .	460	2·08
Butyric acid at . .	350	3·68
Ditto, ditto . .	502	3·07

At the higher temperatures, and at all points above them (until the acid undergoes decomposition), 1 equivalent of the compound yields 4 volumes of vapour; but at low temperatures the vapour volume does not correspond exactly to any specific multiple of the volume of oxygen.

All of the hydrated acids of this group when melted, with the exception of the formic and the acetic, exhibit the properties of an oil, which is imperfectly soluble in water; though some of the lower members of the series are soluble in water to a considerable extent: they are all abundantly soluble both in alcohol and ether.

These acids are regarded as monobasic, but several of them form both neutral and acid salts with the alkalies; a biformiate, a binacetate, and a bistearate of potash, for example, may be eadily obtained. Many of them yield with oxide of lead, not nly the usual neutral salt, but also basic salts, which contain 3 quivalents of oxide of lead for each equivalent of acid. Many f these basic salts are freely soluble in water.

The remarkable relation which these acids bear to the alcohols has already been pointed out (p. 31);—for every alcohol there is a corresponding acid, which may be formed from the alcohol by a regulated process of oxidation, which may sometimes be effected directly—as in the conversion of wine alcohol into vinegar—by the operation of finely divided platinum; but more usually it is necessary to resort to indirect means, such as heating the alcohol with hydrate of potash; in which case hydrogen is eliminated, whilst oxygen enters into the compound, the general form of the equation being:—

$$C_nH_{n+1}O, HO + KO, HO = KO, C_nH_{n-1}O_3 + 4H.$$

The action of gaseous chlorine upon the acids of this group gives rise to the formation of chlorinated acids, in which a certain number of equivalents of the hydrogen is displaced by an equal number of equivalents of chlorine; but the saturating power of the acid is not altered. In many cases more than one chlorinated acid may be formed from the original acid; for example:—

Acetic acid $HO, C_4 H_3 O_3$	Chloracetic acid	$HO, C_4 \left.\begin{matrix}H_2\\Cl\end{matrix}\right\} O_3$
	Trichloracetic acid	$HO, C_4 Cl_3 O_3$
Butyric . $HO, C_8 H_7 O_3$	Bichlorobutyric	$HO, C_8 \left.\begin{matrix}H_5\\Cl_2\end{matrix}\right\} O_3$
	Quadrichlorobutyric	$HO, C_8 \left.\begin{matrix}H_3\\Cl_4\end{matrix}\right\} O_3$
Valeric . $HO, C_{10}H_9 O_3$	Chlorovalerisic (Trichlorovaleric)	$HO, C_{10} \left.\begin{matrix}H_6\\Cl_3\end{matrix}\right\} O_3$
	Chlorovalerosic (Quadrichlorovaleric)	$HO, C_{10} \left.\begin{matrix}H_5\\Cl_4\end{matrix}\right\} O_3$
Stearic . $HO, C_{36}H_{35}O_3$	Chlorostearic	$HO, C_{36} \left.\begin{matrix}H_{25}\\Cl_{10}\end{matrix}\right\} O_3$.

Several of these acids also furnish nitro-acids, when treated with fuming nitric acid; such, for example, as the following:—

Nitropropionic acid .	. $HO, C_6 H_4NO_4, O_3$
Nitrobutyric acid .	. $HO, C_8 H_6NO_4, O_3$
Nitrovaleric acid .	. $HO, C_{10}H_8NO_4, O_3$.

An interesting observation was made by Kolbe regarding the mode in which the salts of these acids are decomposed by the voltaic battery. The first stage of the electrolysis consists in the separation of the salt into two portions; the metal going to the negative plate, whilst the acid and the oxygen travel towards the positive electrode. Here the second stage of the process commences; the oxygen and the acid, reacting upon each other in a definite manner. When, for example, a strong solution of valerate of potash is submitted to the action of four cells of Bunsen's or of Grove's battery, the potassium of the salt is evolved as usual at the negative electrode; and by here decomposing an equivalent of water it immediately forms potash, and liberates an equivalent of hydrogen: but instead of pure valerianic acid being liberated at the positive plate, carbonic acid and a quantity of an ethereal oil, with a portion of undecomposed valerianic acid, are set free. This ethereal oil consists chiefly of tetryl, or butyl = (C_8H_9), the radicle of the fourth alcohol. No oxygen escapes; the valerianic acid having undergone oxidation in the manner indicated by the following symbols:—

$$\overbrace{(KO, C_{10}H_9O_3)}^{\text{Valerate of Potash.}} \text{ yields } \overbrace{K}^{\overset{\text{Cation.}}{+}};\ \overbrace{C_{10}H_9O_4}^{\overset{\text{Anion.}}{-}}:\ \text{and } K + 2\,HO \text{ becomes}$$

$$KO, HO + H;\ \text{whilst } C_{10}H_9O_4 \text{ breaks up into } \overbrace{C_8H_9}^{\text{Tetryl.}} + \overbrace{2\,CO_2}^{\text{Carbonic Acid.}}.$$

Other salts of the same class of acids present analogous phenomena: the acetates yield methyl: the butyrates, trityl (propyl); and, generally, it is found that on decomposing the salts of the stearic group by the voltaic current, they yield at the positive electrode, carbonic acid and the radicle of the alcohol immediately below them in the series. Hence, Kolbe was led to regard the acids of this group as coupled oxalic acids; each acid containing the radicle of the particular alcohol which is separated during its electrolysis; for instance:—

$$\begin{aligned}
&\text{Acetic acid} &&= \overbrace{HO, (C_2H_3)C_2O_3}^{\text{Kolbe.}} &&\text{or Methylformic} &&\overbrace{HO, C_2(C_2H_3)O_3}^{\text{Gerhardt.}}\\
&\text{Propionic} &&= HO, (C_4H_5)C_2O_3 &&\text{or Ethylformic} &&HO, C_2(C_4H_5)O_3\\
&\text{Butyric} &&= HO, (C_6H_7)C_2O_3 &&\text{or Tritylformic} &&HO, C_2(C_6H_7)O_3\\
&\text{Valeric} &&= HO, (C_8H_9)C_2O_3 &&\text{or Tetrylformic} &&HO, C_2(C_8H_9)O_3;
\end{aligned}$$

and so on. Gerhardt prefers to regard them as derivatives of formic acid, in which the hydrogen of the formic acid is displaced by the radicles of the alcohols: this view accords equally well with the results of electrolysis, and is certainly more in harmony with the present state of our knowledge of the mode in which chemical compounds are formed. Such a supposition, however, does not indicate any theory as to the molecular constitution of formic acid itself; it merely states that in whatever way formic acid be constituted, the higher acids of the group are probably similar in their atomic arrangement: and formic acid itself may possibly be an oxide of a radicle which itself contains oxygen. Thus:—

Formic acid would then be . $HO, [C_2(H)O_2]O$
Acetic acid „ . $HO, [C_2(C_2H_3)O_2]O$
Propionic acid „ . $HO, [C_2(C_4H_5)O_2]O$.

Some difficulty is experienced in procuring the soluble salts of the higher fatty acids in a state of purity; since few of them crystallize readily from their aqueous solutions. The baryta salts when soluble, however, generally admit of being procured in well-defined forms.

The soda salts of this group of acids are all soluble in hot water, and are therefore easily prepared by boiling the fatty acid with a slight excess of the alkali. This excess of alkali may be removed from the soda salts of the higher terms of the series, by taking advantage of their insolubility in a concentrated solution of chloride of sodium; for as soon as the solution of the soap is poured into strong brine, the soda soap is separated in the form of a curdled granular mass, which can be easily collected on a linen filter and pressed, whilst the excess of soda remains in solution with the chloride of sodium. The coagulated soap is then to be re-dissolved in water, and salted out once or twice more: finally, the soda salt may be purified from the chloride of sodium by re-crystallization from alcohol.

The foregoing process cannot be adopted with the potash salts, since the potash soaps are decomposed when mixed with chloride of sodium, a soda soap being formed whilst chloride of potassium remains in solution. Chloride of potassium cannot be substituted for chloride of sodium in salting out, since the soaps are not insoluble in a solution of chloride of potassium.

The method to be used in the preparation of the pure potash salts consists, therefore,—in boiling the acid with an excess of carbonate of potash, evaporating the solution to dryness, and then separating the potash salt from the excess of carbonate by dissolving the soap in alcohol: on evaporation of the alcoholic solution, the potash salt of the oily acid may generally be obtained in crystals.

The insoluble soaps may be procured by double decomposition; a pure and rather dilute solution of the potash or of the soda salt being mixed with a dilute solution of a salt of the metallic oxide, such as sulphate of copper, acetate of lead, or nitrate of silver; according as a compound of copper, of lead, or of silver, is desired.

The following table indicates the composition of the acids of the stearic series, and the melting point of each acid, with the source whence it is obtained:—

Acids.	Formulæ.	Melting point ° F.	Boiling point ° F.	Whence obtained.	
Melissic . .	HO, $C_{60}H_{59}O_3$	192		Bees' wax.	
Cerotic . .	HO, $C_{54}H_{53}O_3$	174		Bees' wax.	
Arachidic .	HO, $C_{40}H_{39}O_3$	167		Butter; oil of ground nut.	
Stearic . .	HO, $C_{36}H_{35}O_3$	159		Most solid animal fats.	
Palmitic .	HO, $C_{32}H_{31}O_3$	143.8		Palm oil; butter; bees' wax, &c.	
Myristic .	HO, $C_{28}H_{27}O_3$	129		Nutmeg butter; cocoa-nut oil, &c.	
Lauric . .	HO, $C_{24}H_{23}O_3$	110		Cocoa-nut oil; berries of the bay tree.	
Rutic . .	HO, $C_{20}H_{19}O_3$	86		Butter; oil of rue by oxidation	
Pelargonic .	HO, $C_{18}H_{17}O_3$		500	Leaves of the geranium.	By oxidation of oleic acid with nitric acid.
Caprylic .	HO, $C_{16}H_{15}O_3$	59	457	Butter; cocoa-nut oil.	
Œnanthylic	HO, $C_{14}H_{13}O_3$	below 0°	298?	Castor oil by distillation, &c.	
Caproic . .	HO, $C_{12}H_{11}O_3$		392	Butter.	
Valeric . .	HO, $C_{10}H_9O_3$	below 0	347	Valerian root; oxidation of fousel oil.	
Butyric . .	HO, $C_8H_7O_3$	below 0	314	Butter; fermentation of lactic acid, &c.	
Propionic .	HO, $C_6H_5O_3$		284	Fermentation of glycerin, &c.	
Acetic . .	HO, $C_4H_3O_3$	63	243	Distillation of wood; oxidation of alcohol, &c.	
Formic . .	HO, C_2HO_3	21	221	Red ants; distillation of oxalic acid; and oxidation of amylaceous and other organic bodies.	

Melissic and *cerotic* acids have been already described (1135). *Arachidic* or *butic* acid does not appear to have been obtained from butter in a state of perfect purity; but a crystallizable fatty acid having the composition assigned to it in the Table, has been extracted from the oil obtained from the seeds of the *Arachis hypogæa*, the ground-nut oil of Western Africa.

(1154) STEARIC ACID (HO, $C_{36}H_{35}O_3$).—This important fatty acid is liberated during the saponification of all the fats which contain stearin. Until recently it was regarded as a dibasic acid, and its formula was represented as ($2\,HO, C_{68}H_{66}O_5$). It may, however, with care, be distilled without decomposition, and further experiments by Heintz and others have shewn that it belongs to the same series of acids as the palmitic, which it greatly resembles. The *bassic acid,* which Hardwich extracted from the oil of the *Bassia latifolia,* and found to possess the formula ($HO,C_{36}H_{35}O_3$), is pure stearic acid.

Stearic acid may be obtained by saponifying mutton suet, and decomposing the hot solution of the soap with hydrochloric, or still better, with tartaric acid. The oily acids are next to be submitted to pressure between hot plates, by which means a large portion of the oleic acid is separated: the solid residue is then to be recrystallized from alcohol, three or four times, and afterwards from ether, until the fusing point becomes constant at 159°. The ethereal solution, if allowed to cool very slowly, deposits the acid in beautiful colourless, transparent, rhombic plates. When fused it presents the appearance of a colourless oil, destitute of taste or odour; and, on solidifying, it concretes into a white crystalline mass, which is insoluble in water, but freely soluble in hot alcohol: this solution reddens litmus.

Stearates.—Stearic acid forms both acid and neutral salts. The stearates of the alkalies are soluble in a small quantity of water, and in alcohol; a mixture of alcohol and ether, of sp. gr. 0·750, also dissolves them, and deposits them in crystals on cooling. When an aqueous solution of neutral stearate of potash or of soda is largely diluted with water, the liquid becomes turbid, and a copious separation of silky crystalline plates of an acid stearate of the base is occasioned. Chevreul, who has carefully examined this decomposition, finds that it is not an isolated case, but that generally, when a salt is formed by the union of a base soluble in water with an acid which is insoluble, the neutral salt so obtained is decomposed by water, with the precipitation of an insoluble acid salt, while a portion of the base remains in solution.

Stearate of soda is the basis of ordinary hard soap. The soluble stearates are separated from their solution in water by the addition of a large excess of soda or of potash. Chloride of sodium also causes their immediate coagulation; and some other salts have a similar effect: advantage is taken of this fact to separate soap from glycerin and other impurities in the operation of soap-making.

The other stearates are insoluble; those of baryta and lime are crystalline, and insoluble in alcohol. Stearate of magnesia is fusible, and may be dissolved by boiling alcohol. Stearate of lead is easily formed by adding a solution of acetate of lead to one of stearate of soda: it is a heavy amorphous precipitate, fusible at about 260°, sparingly soluble in alcohol and in ether, but readily soluble in oil of turpentine: stearate of lead is one of the constituents of the ordinary lead plaster.

Stearic acid, when submitted for some weeks to a current of chlorine, at a temperature of 212°, loses a portion of its hydrogen, and becomes converted into a yellowish, transparent, chlorinated compound, of a resinous aspect, in which Hardwich found that 10 equivalents of hydrogen had been displaced by 10 equivalents of chlorine, forming *chlorostearic acid* ($HO, C_{36}H_{25}Cl_{10}O_3$).

When stearic acid is boiled for some days with nitric acid, it is gradually converted into suberic and succinic acids (1180, 1181). It has been stated that it may be converted into margaric acid by gently heating it for a short time with nitric acid, but Heintz has shewn that this is an error.

(1155) PALMITIC ACID ($HO, C_{32}H_{31}O_3$).—This acid is obtained most readily from palm oil, the solid portion of which consists chiefly of the glycerin compound of palmitic acid, and which, when long kept, often contains the free acid in large quantity, amounting in some instances to one-third of its weight. Under these circumstances the oil contains a considerable quantity of uncombined glycerin. Palmitic acid may also be procured by the saponification of spermaceti: according to Heintz, it is likewise present in human fat, in the solid constituent of olive oil, and generally in substances which have been described as yielding margarin. It is likewise one of the products of the decomposition of oleic acid when this body is fused with twice its weight of hydrate of potash:—

$$\overbrace{HO, C_{36}H_{33}O_3}^{\text{Oleic Acid.}} + 2\,(KO, HO) = \overbrace{KO, C_{32}H_{31}O_3}^{\text{Palmit. Potash.}} + \overbrace{KO, C_4H_3O_3}^{\text{Acet. Potash.}} + 2\,H.$$

Palmitic acid, after repeated crystallization from alcohol, appears as a tasteless white fat, which may be obtained in tufts of delicate needles, fusible at 143°·6. It may, with care, be distilled without undergoing decomposition.

The neutral palmitates of the alkalies are readily soluble in hot water, and form a solution which gelatinizes on cooling. They are sparingly soluble in cold alcohol, but freely so in boiling alcohol: this solution deposits the salts in crystals on cooling. The aqueous solutions of the neutral palmitates, when largely diluted with water, are decomposed in a manner similar to those of the stearates, into an insoluble acid salt, whilst a portion of the [illegible] remains in solution.

(1156) MARGARIC ACID ($HO, C_{34}H_{33}O_3$).—The existence of this acid has recently been denied by Heintz, who states that the body hitherto described under this name is in reality a mixture of stearic and palmitic acids. In order to prepare the substance formerly designated as margaric acid, Marseilles, or olive-oil soap, is to be dissolved in boiling water, and mixed with a solution of chloride of calcium; a precipitate of mingled oleate and margarate of lime is thus obtained, which after being dried is pulverized and digested in cold ether, so long as anything is dissolved: the oleate of lime is thus brought into solution, whilst the margarate is left behind. The margarate is then decomposed by boiling it with hydrochloric acid, and the oily acid which separates is thoroughly washed and recrystallized from alcohol; as thus obtained it melts at 140° F. Heintz, however, states that the acid so obtained may be separated into stearic and palmitic acid, by repeatedly crystallizing it from alcohol; the melting point may thus be raised till it reaches 159°, the fusing point of stearic acid. A better plan consists in adding to a boiling solution of the acid in alcohol a boiling solution of acetate of lead, or of acetate of baryta, containing a quantity of the baryta, or lead salt, amounting to two-sevenths of the weight of the fatty acid. As the liquid cools, a precipitate is obtained, which is to be collected upon a filter. This portion contains the whole of the stearic acid, whilst most of the palmitic acid remains in solution; the filtered liquid is now to be precipitated by an excess of the baryta or lead salt. This latter precipitate contains the palmitic acid; it may be decomposed by hydrochloric acid, and recrystallized from alcohol till its melting point remains fixed at 143°·6. If necessary, it may be again submitted to a partial precipitation with acetate of lead, or of baryta.

Although the melting point of stearic acid is 159°, and that of palmitic acid is 143°·6, Heintz finds that a mixture of the two acids melts at a lower temperature than either of them separately; and if 9 or 10 parts of palmitic acid be fused with 1 part of stearic acid, a mass is obtained which solidifies at 140°; which corresponds to the fusing point of the so-called margaric acid.

(1157) *Myristic acid* ($HO, C_{28}H_{27}O_3$) is comparatively unimportant; it is furnished by nutmeg butter, and fuses at 129° (Heintz).

Lauric acid ($HO, C_{24}H_{23}O_3$), fusing point 110° (Heintz), was first extracted from the soft green fat of the bay berries (*Laurus nobilis*), but it has since been found in cocoa-nut oil (Georgey), as well as in the pichurim nut and in cacao butter.

(1158) *Capric*, or as it has been more conveniently termed, *rutic acid* ($HO, C_{20}H_{19}O_3$), is a volatile fatty acid which possesses many interesting relations to other bodies. It was discovered by Chevreul amongst the products of the saponification of butter; but it is also furnished by the oxidation of oleic acid by nitric acid, and Gerhardt has procured it readily by acting upon oil of rue with fuming nitric acid; oil of rue ($C_{20}H_{20}O_2$), having in fact the composition of the aldehyd of capric acid: during the oxidation of oil of rue by nitric acid, a portion of pelargonic acid is usually formed at the same time. Capric acid is also contained in small quantity in the fatty acids of the cocoa-nut oil. Capric acid crystallizes in colourless needles, which are fusible at 86°; it has a slight odour of the goat. This acid is sparingly soluble in boiling water, but it separates completely, in glistening plates, as the liquid cools; its taste is sour and burning. It is soluble in alcohol in all proportions: when distilled it is liable to undergo partial decomposition. Capric acid is generally purified by causing it to combine with baryta; the salt thus obtained crystallizes in brilliant plates: it is soluble to a considerable extent in boiling water, but requires 200 parts of cold water for solution.

(1159) *Pelargonic Acid* ($HO,C_{18}H_{17}O_3$).—This acid is comparatively unimportant: it was originally extracted from the leaves of the geranium, by distilling them with water, purifying the oil which floats on the surface by neutralizing it with hydrate of baryta, and heating the mixture to drive off a volatile oily body which comes over with the acid. The pelargonate of baryta is afterwards decomposed by an acid. Pelargonic acid may also be prepared by heating oil of rue with an equal measure of nitric acid which has been diluted with its own bulk of water; and it is also produced by the oxidation of oleic acid by the same reagent. *Pelargonic anhydride* ($C_{18}H_{17}O_3, C_{18}H_{17}O_3$) is a colourless oil which solidifies at 32°, and has a disagreeable odour of rancid butter: it is obtained by acting upon pelargonate of baryta with oxychloride of phosphorus. *Hydrated pelargonic* acid is a colourless oil which is nearly insoluble in water, but soluble in alcohol and ether: it has a faint unpleasant smell; at 500° it boils, and may be distilled unchanged: according to Delffs it is identical with the œnanthic acid of Liebig and Pelouze.

(1160) *Caprylic acid* ($HO, C_{16}H_{15}O_3$), *Sp. gr. of vapour* 5·31, was one of the volatile acids obtained by Chevreul during the saponification of butter; it is found likewise in cocoa-nut oil, as well as amongst the products of the oxidation of oleic acid by nitric acid.

Caprylic anhydride ($C_{16}H_{15}O_3$, $C_{16}H_{15}O_3$) is a limpid oil of a disagreeable odour, which burns with a luminous flame: it becomes solid in the cold produced by a mixture of ice and salt. *Hydrated* caprylic acid becomes solid at about 54°, it melts at 58° or 59°, and boils and may be distilled at 457°: it is but sparingly soluble in water even at a temperature of 212°. It is best prepared by decomposing the caprylate of baryta with sulphuric acid: caprylate of baryta is insoluble in alcohol and in ether, but is dissolved by twice its weight of boiling water; it crystallizes from its aqueous solution in anhydrous colourless plates, which are deposited in rounded nodular masses. Caprylic acid is usually accompanied by rutic acid, but since the caprylate of baryta is more soluble than the rutate of this base, the acids may be separated by converting them into baryta salts and then crystallizing them.

(1161) *Œnanthylic Acid* ($HO,C_{14}H_{13}O_3$).—This acid is obtained as one of the products of the oxidation of oleic acid by means of nitric acid. It is also produced during the destructive distillation of castor oil; but it is most readily obtained by heating one part of castor oil in a retort with two parts of concentrated nitric acid diluted with twice its volume of water. A brisk reaction occurs; the mixture must be maintained at a boiling temperature for a few hours, and the products which distil over must be mixed with water, when an oily stratum of œnanthylic acid will rise to the surface; it must be again distilled with water, and may be obtained as a monohydrate by distilling the liquid from fused phosphoric acid.

Œnanthylic anhydride ($C_{14}H_{13}O_3$, $C_{14}H_{13}O_3$) may be obtained as an oily liquid of sp. gr. 0·92, by distilling œnanthylate of potash with oxychloride of phosphorus. *Hydrated* œnanthylic acid may be exposed to a cold of 0° without becoming solid; it boils and may be distilled at 298°, but it undergoes partial decomposition during the operation. One of its most characteristic salts is the œnanthylate of copper, which crystallizes in beautiful green needles; these are soluble in alcohol, but nearly insoluble in water.

(1162) *Caproic Acid* ($HO, C_{12}H_{11}O_3$); *Sp. gr. of vapour* 4·26.—This acid is liquid at ordinary temperatures: it has a characteristic odour of acid sweat, and has a pungent and sweetish taste; the concentrated acid bleaches those parts of the tongue which it touches. It boils at about 392°, and may be distilled unchanged. Water dissolves it to a small extent. Caproic acid is obtained in small quantity by the saponification of butter, or of cocoa-nut oil, and it is amongst the volatile products of the oxidation of oleic by nitric acid. It may be obtained from butter by pressing out the portion which remains liquid at 60°, then saponifying this oil and distilling the soap with sulphuric acid; rutic, caprylic, caproic, and butyric acids are thus obtained in the liquid which passes over. The distillate is to be neutralized with baryta, which forms a soluble caproate, whilst the caprylate and rutate are nearly insoluble. The caproate and butyrate are separated by crystallization, the caproate assuming the form of delicate, brilliant, anhydrous needles, if the solution be evaporated above 86°, whilst if left to spontaneous evaporation it forms hexagonal plates which effloresce in the atmosphere. Anhydrous caproate of baryta, if distilled with perchloride of phosphorus, yields *caproic anhydride* ($C_{12}H_{11}O_3$, $C_{12}H_{11}O_3$), in the form of a colourless neutral oil, which floats on water, by which it is rapidly converted into the hydrated acid. Caproate of silver is sparingly soluble, but most of the other salts of the acid are readily dissolved by water.

(1163) VALERIC, OR VALERIANIC ACID (HO, $C_{10}H_9O_3$); *Sp. gr. of liquid* 0·937, *of vapour* 3·66.—This compound appears to be identical with the *phocenic* acid obtained by Chevreul from some of the fish oils. It occurs also (associated with a peculiar essential oil) in the root of the valerian; it is likewise present in the berries of the guelder-rose (*Viburnum opulus*). If valerian root be distilled with water acidulated with dilute sulphuric acid, valeric acid passes over into the receiver: its quantity may be increased by digesting the root with a mixture of dilute sulphuric acid and bichromate of potash, since the valerian root contains a compound (valerol, $C_{12}H_{10}O_2$), which by oxidation becomes converted into valeric acid. Valeric acid is also a frequent product of the oxidation of oleic acid and of other fatty acids; it is likewise often present in decaying cheese, but it is most readily obtained by the action of oxidizing agents on amylic alcohol. If the vapours of fousel oil be sent through a tube, filled with a mixture of lime and hydrate of soda and heated to 400°, valerate of soda is produced, and hydrogen, mixed with carburetted hydrogen, is evolved. When cold, the mass must be plunged at once into water to prevent it from taking fire by access of air; and the solution must be distilled with dilute sulphuric acid; valeric acid then passes over into the receiver. A still easier method of preparing it consists in distilling fousel oil with a mixture of dilute sulphuric acid and bichromate of potash; valeric acid mixed with valerate of amyl ($C_{10}H_{11}O$, $C_{10}H_9O_3$) passes over, and the latter may be decomposed by potash into valerate of potash and fousel oil. The valerate of potash when distilled with sulphuric acid furnishes pure valeric acid.

Valeric acid is a limpid colourless oil, which remains liquid at 0°. It has a powerful odour allied to that of valerian root, and a burning taste. It boils at 347°, and may be distilled without change. It is sparingly soluble in water, but is soluble in alcohol and ether in all proportions: it is also freely soluble in strong acetic acid. Valeric acid resembles the acetic in its property of forming a second hydrate ($HO, C_{10}H_9O_3, 2\ Aq$), which is obtained when the acid is liberated by a stronger acid from an aqueous solution of its salts. *Valeric anhydride* ($C_{10}H_9O_3, C_{10}H_9O_3$; sp. gr. 0·934) is a colourless, mobile liquid, with an agreeable odour of apples; it boils at 419°, and gives off a vapour of sp. gr. 6·23: the alkalies in the presence of water rapidly convert it into a hydrate. This compound is easily obtained by allowing one part of oxychloride of phosphorus to fall drop by drop upon six parts of dry valerate of potash; washing the product with a weak solution of carbonate of soda, and then dissolving out the anhydride with ether: the ethereal solution is agitated with fused chloride of calcium in order to remove water; and on expelling the ether by heat, the anhydride is left in a state of purity.

The valerates when dry are destitute of odour, they have a sweetish taste, and are easily recognized by the peculiar smell of valerianic acid which they emit when heated with dilute sulphuric acid. These salts, with the exception of the valerate of silver and of suboxide of mercury, are soluble in water, and many of them are also soluble in alcohol. Those of the alkalies are deliquescent, and crystallize with difficulty; they fuse readily on the application of a moderate heat. Valerate of baryta crystallizes in prisms which are brittle. Valerate of zinc crystallizes in plates; this salt, as well as some others of the valerates, has been used medicinally.

Chlorine acts upon valeric acid by displacing a portion of its hydrogen; by this means two new substitution compounds may be formed. Both of these bodies retain the monobasic character of valerianic acid. They were termed by Dumas, *chlorovalerisic* ($HO, C_{10}H_6Cl_3O_3$) and *chlorovalerosic* ($HO, C_{10}H_5Cl_4O_3$) acids; both of them form stable, well-defined salts.

When valeric acid is boiled for several days with concentrated nitric acid it becomes decomposed, and a great part is converted into *nitrovaleric acid* ($HO, C_{10}H_8(NO_4)O_3$), which is volatile without decomposition; it crystallizes in beautiful rhomboidal tables, and forms definite salts.

(1164) **Butyric Acid** ($HO, C_8H_7O_3$); *Sp. gr. of liquid at* 32°

0·9886, *of vapour* 3·07.—This acid is a liquid which, at 59°, has the sp. gr. 0·973; it remains fluid at −4° F., and volatilizes at ordinary temperatures with a strong smell of rancid butter; it boils at 314°·6 F. (Kopp), and may be distilled unchanged. Butyric acid has a sharp acrid taste, and is readily soluble in water, alcohol, and ether: the addition of a solution of hydrochloric acid or of chloride of calcium to its aqueous solution causes the butyric acid to separate and rise to the surface. The acid is easily obtained in a state of purity by distilling three parts of the butyrate of lime with twelve parts of water and one of concentrated hydrochloric acid: about one part of liquid should be distilled over. If the distillate be digested upon an excess of chloride of calcium, the solution which is formed separates into two layers, the upper one of which contains the butyric acid: it must be decanted into a retort and distilled: the first portions which pass over are aqueous, but when the temperature rises to 327° (Gélis and Pelouze), the acid passes over in the concentrated form ($HO, C_8H_7O_3$). *Butyric anhydride* $C_8H_7O_3, C_8H_7O_3$); *Sp. gr. of liquid at* 55°·0·978, *of vapour* 5·38.—This body may be obtained by distilling a mixture of five parts of chloride of benzoyl, and eight of dry butyrate of soda: it forms a colourless, very mobile liquid, with an odour which resembles that of the pine apple. It boils at 374°. When exposed to the air it absorbs moisture and acquires the repulsive odour of the hydrated acid.

Butyrates.—Butyric acid is monobasic. Its salts when dry are without odour; but when moist they have a smell of rancid butter. Most of them are very freely soluble; when reduced to powder, and thrown upon water, they are dissolved with a rapid gyratory motion. *Butyrate of baryta* crystallizes, by spontaneous evaporation, in long prisms, with four equivalents of water; when formed by the cooling of a hot solution it retains only two equivalents of water.* *Butyrate of zinc* crystallizes in pearly tables, which when heated to 212° fuse and then lose part of their acid, after which a portion of the salt undergoes sublimation in the anhydrous form. With *lead*, butyric acid forms two salts, one of which is neutral, while the other contains three equivalents of base. The butyrates of *suboxide of mercury* and of *silver* are sparingly soluble; they crystallize in brilliant plates. But the most characteristic salt of butyric acid is the *butyrate of lime*, which forms fusible colourless needles, which are rendered anhydrous by a temperature of 284°: this salt is much less soluble in boiling water than it is at ordinary temperatures, and when its aqueous solution is boiled, a large proportion of the salt is precipitated, and is redissolved as the liquid cools. Chlorine acts readily upon butyric acid in the sunlight, and forms two substitution acids which are analogous to butyric acid, and which yield corresponding monobasic salts; these acids are:—

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* On one occasion I obtained it crystallized in anhydrous square tables, presenting the appearance of the square base of the octohedron. They were, however, in reality macled crystals formed by the junction of two nearly rectangular rhombic tables. In other cases the salt forms fibrous crystals which are also anhydrous.

Bichlorobutyric	$HO, C_8H_5Cl_2O_3$
Quadrichlorobutyric . . .	$HO, C_8H_3Cl_4O_3$.

Nitric acid converts the butyric into *nitrobutyric* acid ($HO, C_8H_6NO_4, O_3$.)

Butyric acid exists ready formed in certain fruits, and it is one of the products of oxidation of azotised matters, such as fibrin or casein, when treated with oxide of manganese and sulphuric acid; it is also obtained amongst the results of the action of nitric upon oleic acid. All substances which furnish lactic acid may be made to yield the butyric; and it is frequently developed during the fermentation or decay of many mucilaginous and amylaceous roots, such as the potato and the mallow. Butyric acid may be obtained at pleasure in large quantities, by the following method of fermenting sugar discovered by Pelouze and Gélis (*Ann. de Chimie*, III. x. 434). A solution of 4lb. of sugar in a quantity of water sufficient to form a solution of sp. gr. 1·070, is mixed with a quantity of poor cheese, which in its dry state would contain casein to the extent of one-eighth of the weight of the sugar used, and 2lb. of chalk; the whole is then exposed for some weeks to a temperature ranging between 80° and 90° F. The liquid speedily becomes ropy, lactic acid is formed abundantly, and combines with the lime, but the lactate of lime in turn undergoes decomposition; when this second reaction commences, a mixture of carbonic acid and hydrogen escapes from the fermenting mass, and butyrate of lime is formed in abundance. This reaction is explained by the following equation:—

$$2\overbrace{HO, C_{12}H_{10}O_{10}}^{\text{Lactic Acid.}} = \overbrace{HO, C_8H_7O_3}^{\text{Butyric Acid.}} + 4\,CO_2 + 4\,H.$$

(1165) *Propionic,* Propylic, Metacetic, or Metacetonic Acid* ($HO, C_6H_5O_3$).—This acid is formed in a variety of ways; for example—it is one of the products of the oxidation of oleic acid; and it is also obtained by the action of potash upon hydrocyanic ether. In the latter case, ammonia is liberated and propionate of potash is formed:—

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* From πρῶτος first, πίων fat, because the first or simplest in the series of the true fatty acids.

$$\overbrace{C_4H_5,C_2N}^{\text{Cyanide of Ethyl.}} + 2\,HO + KO,HO, = \overbrace{KO,C_6H_5O_3}^{\text{Propionate of Potash.}} + H_3N;$$

a concentrated alcoholic solution of potash is to be heated in a tubulated retort, and cyanide of ethyl added drop by drop; the distillate is to be returned into the retort until the odour of cyanide of ethyl has disappeared: the residue of propionate of potash, when distilled with syrupy phosphoric acid, yields pure propionic acid.

Strecker has likewise observed the formation of this acid by the fermentation of a mixture of lactate of lime and mannite, which had been set aside with the view of procuring butyric acid. Crude tartrate of lime in warm weather frequently undergoes a species of fermentation, and furnishes propionic acid. The acid is also produced during the fermentation of glycerin (1147). Metacetone (C_6H_5O; 924) when oxidized with a mixture of bichromate of potash and sulphuric acid, also yields the acid, and it derived its name of metacetonic acid from this circumstance. Propionic acid, when prepared from these sources, is liable to be contaminated with acetic and other acids homologous with the acetic. These may be removed by saturating the distilled liquid with carbonate of soda, and evaporating to the crystallizing point; the acetate of soda crystallizes out, whilst the propionate remains in the mother liquor, from which propionic acid may be procured by distillation with sulphuric acid.

Hydrated propionic acid ($HO, C_6H_5O_3$) crystallizes in plates which melt on the application of a gentle heat; at a temperature of 284° it boils and may be distilled: it has a powerfully acid taste, and a pungent odour which is intermediate between that of butyric and of acrylic acids. Propionic acid is largely soluble in water, but, when this liquid is saturated with it, the excess of the acid floats like an oil upon the surface.

Most of the propionates are soluble and crystallizable. The propionates of *potash* and of *soda* are deliquescent. *Propionate of lime* is efflorescent, but very soluble. *Propionate of baryta* is anhydrous, and very soluble; it crystallizes in prisms, which when thrown into water are dissolved with a gyratory motion. *Propionate of copper* ($CuO, C_6H_5O_3, Aq$) crystallizes in oblique prisms, which are readily soluble in alcohol, but very slightly so in water. *Propionate of silver* is anhydrous, and less soluble than the acetate; it crystallizes in tufts of short needles, and blackens by exposure to light; but the acetate and the propionate of silver cannot be separated by crystallization, for they unite and form a double salt, which is deposited from a hot solution in brilliant dendritic needles.

A *nitro-propionic acid,* $\mathrm{HO,\ C_6}\left.\begin{matrix}\mathrm{H_4}\\ \mathrm{NO_4}\end{matrix}\right\}\mathrm{O_3}$, may be obtained as a heavy yellow, sparingly soluble oil, by treating butyrone, $C_{14}H_{14}O_2$, with nitric acid. Its salts detonate feebly when heated.

(1166) ACETIC ACID ($HO, C_4H_3O_3$)—This acid was one of the earliest known of the organic acids, and it is one of the most important. In a dilute form, mixed with various impurities of vegetable origin, it constitutes ordinary vinegar, which rarely contains more than 5 per cent. of the anhydrous acid.

Preparation.—The existence of acetic acid in the juices of plants has not been satisfactorily proved, but it is formed artificially in a variety of processes.

1. A large quantity is furnished during the destructive distillation of wood in iron retorts. The wood is usually placed in these retorts in loose iron cases, by which means the charge can be rapidly introduced without loss, while the retort is still hot, and the charcoal can be withdrawn when the distillation is complete. The harder kinds of wood, particularly the ash and beech, are those which yield it most abundantly: the crude acid thus obtained is called in the arts, *pyroligneous acid.* A large quantity of tarry matter comes over during the operation, accompanied also by volatile and inflammable bodies, among which wood-spirit and acetone predominate. These bodies are condensed in suitable receivers, whilst a considerable quantity of combustible gases, including hydrogen and marsh gas, are directed into the furnace, where they serve as fuel, and aid in heating the retorts. As soon as the gases cease to escape, the loose iron cylinders containing the wood are withdrawn, and immediately closed with an air-tight cover, so as to allow the charcoal to cool excluded from the atmosphere. The crude acid liquid which has been collected in the condenser is decanted from the tar, and, when submitted to distillation, furnishes *wood naphtha,* which constitutes the more volatile portions; afterwards the acetic acid is collected; the latter, however, is always accompanied by tarry matters; in order to get rid of these, the liquid is neutralized by the addition of carbonate of lime, or carbonate of soda, and the crude acetate thus obtained is cautiously roasted at a gentle heat to expel

the tarry matters, and is afterwards recrystallized and submitted to distillation with sulphuric or with hydrochloric acid. The greater part of the acetic acid employed in the arts in this country is obtained by this method. M. Mollerat, taking advantage of the insolubility of sulphate of soda in acetic acid, obtains a nearly pure acid at once, by allowing sulphuric acid to flow into a deep vessel containing the acetate of soda, in the proportion of 34lb. or 36lb. of oil of vitriol for every 100lb. of acetate of soda. The sulphuric acid is caused to flow quietly under the salt without mixing with it, in order that the heat developed by the reaction shall be very moderate; the materials are then slowly mixed, and after standing for a few hours the decomposition is complete; the contents of the vessels gradually separate into two layers, the upper one containing the concentrated acetic acid, and the lower one consisting of sulphate of soda. The acetic acid is drawn off with a syphon, and is afterwards rendered perfectly pure by distillation.

2. In countries where alcohol is cheap, and particularly in Germany, dilute acetic acid is prepared on a large scale by the oxidation of alcohol in the manner already described (972), the diluted spirit being made to trickle slowly over a large surface of wood shavings contained in vats of suitable construction.

(1167) 3. *Vinegar.*—The vinegar which is most esteemed for culinary purposes is that prepared from wine; it is extensively manufactured in France, from the acescent varieties of wine. The wine is introduced into large casks capable of containing about 100 gallons each: they are arranged in rows in a shed, the temperature of which is kept at from 75° to 85°. The upper part of these casks is partially open to allow the access of air. A certain quantity of good vinegar at a boiling temperature is then placed in each cask, and every eight days a few gallons of fresh wine are added until the casks are about two-thirds full. In about a fortnight the acidification is complete, a few gallons of the vinegar are then drawn off from each cask, and the vessels are again filled up to the same extent with a fresh quantity of the wine to be acidified. It is found that this process takes place much less rapidly in new casks than in those which have been used for this purpose for some time. A quantity of a gelatinous conferva becomes developed in them, and this substance, which has received the name of *mother of vinegar,* favours the absorption of oxygen by the alcohol, in a manner which is supposed to be somewhat analogous to that in which platinum black acts under similar circumstances (859).

The following method of preparing vinegar, contrived by Boerhaave, is still practised extensively:—Two large vats are each provided with a false bottom supported at a height of about a foot above the floor of the vessel. Each vat is filled with vine cuttings, and *rapes*, or the foot stalks and skins of grapes; the vats are then charged with wine, one of them being completely filled, and the other only half filled. In this state the two vessels are left for at least twenty-four hours at a temperature of 75°. At the expiration of this time the vat which had been left only half full is filled up from the full one, and thus every twenty-four hours a portion of the wine is transferred alternately from one vat to the other. The acetification goes on most rapidly in the vat which is only half full, and in this a sensible elevation of temperature may be perceived after the first three or four days, but it should not be allowed to rise beyond 80°. The process requires from a fortnight to three weeks for its completion, according to the temperature of the atmosphere at the time. The vinegar is finally drawn off into settling casks, and when clear is fit for use.

4. Infusion of malt, weak solutions of sugar, and even mixtures of starch with yeast, furnish very good vinegar. Malt vinegar is the principal variety of vinegar employed for domestic purposes in England. According to Ure, a good vinegar for domestic purposes may be prepared by adding to each gallon of a syrup composed of 1¼lb. of sugar and 1 gallon of water, a quarter of a pint of yeast. If kept for three days at a temperature of 75° or 80°, it will be sufficiently acidified to allow of being drawn off into the ripening cask, where 1 ounce of bruised raisins and 1 ounce of crude tartar are to be added to each gallon of liquor. When the sweet taste has quite disappeared it should be drawn off into bottles and corked down tightly; it is stated that such vinegar will contain 5 per cent. of pure acetic acid. In all cases where vinegar is formed by the oxidation of alcohol, it is necessary to favour the absorption of oxygen and the process of acetification by the presence of yeast, or of some albuminous matter such as is naturally contained in solution in the juices of plants or in vegetable infusions made at ordinary temperatures. A pure dilute solution of alcohol is not susceptible of acidification by exposure to the air.

Vinegar prepared by the foregoing methods from fermented or fermentable liquors contains a large quantity of foreign matters, from nearly all of which it may be freed by simple distillation: the acid liquid which comes over constitutes what is known in pharmacy as *distilled* vinegar. The strength of any vinegar is best ascertained by determining the quantity of anhydrous carbonate of soda which a given weight of it will neutralize: 100 grains of carbonate of soda corresponding to 96·2 grains of the anhydrous acid. Care must be taken to ascertain the absence of sulphuric or of any other acid when operating in this way. Commercial vinegar is allowed by law to contain $\frac{1}{1000}$th of its weight of sulphuric acid; the presence of which prevents the vinegar from becoming mouldy.

Monohydrated acetic acid is best procured in a pure form by distilling acetate of soda with sulphuric acid, diluted with one-fourth of its weight of water. Either binacetate of potash or acetate of copper, when submitted to distillation without any addition, also furnishes the concentrated acid with facility.

(1168) *Properties of Acetic Acid.*—Normal acetic acid ($HO, C_4H_3O_3$ *sp. gr.* 1·063 at 62°) is liquid at temperatures above 55° F., at which temperature it crystallizes in radiating tufts of plates. It may be mingled in all proportions with water, and its density increases on dilution, until it contains three equivalents of water, when its density is 1·079. If it be further diluted, the density diminishes according to the ordinary law. In consequence of this anomaly, monohydrated acetic acid, and the same acid diluted with an equal weight of water, possess each the sp. gr. 1·063. The concentrated acid has a sharp aromatic taste, and a peculiar pungent odour; it blisters the skin if applied to it for a sufficient length of time. It boils at 243°, and may be distilled unchanged. The vapour of this acid is inflammable, producing by its combustion water and carbonic acid. The vapour of acetic acid exhibits an anomalous dilatation when exposed to a gradually rising temperature:—

At 69° the density is 3·95
At 257° „ „ „ 3·2
At 320° „ „ „ 2·48
At 392° the density is 2·22
At 446° „ „ „ 2·09
At 460° „ „ „ 2·08;

and beyond this it undergoes no further alteration until the acid is itself decomposed. At 446° and upwards, 1 equivalent of the acid follows the usual law of yielding 4 volumes of vapour (Bineau).

Acetic anhydride ($C_4H_3O_3, C_4H_3O_3$) *Sp. gr. of liquid at* 69°, 1·073; *of vapour* 3·47.—This compound was obtained by Gerhardt by several methods; but the easiest consists in distilling three parts of oxychloride of phosphorus with eight of anhydrous acetate of potash, returning the liquid which passes over upon the residue and redistilling, until the odour of the chloride has disappeared;

finally the liquid is rectified. When pure it boils at 279°·5, and is a colourless, very mobile liquid of high refracting power; it possesses a very pungent smell, resembling that of acetic acid, combined with that of the hawthorn blossom. It emits a vapour which is extremely irritating to the eyes. Acetic anhydride does not mix immediately with water, but sinks through it in oily drops, which become slowly dissolved, evolving heat, and forming the ordinary hydrated acid. This anhydride gradually absorbs moisture from the air, and becomes converted into hydrated acetic acid. Potassium acts rapidly upon it, an inflammable gas being given off, and the compound being by degrees converted into a crystalline mass of anhydrous binacetate of potash [$(KO, 2\ C_4H_3O_3)$]. The same compound is also formed by dissolving dry acetate of potash in the anhydride.

(1169) *Acetates.*—Acetic acid is monobasic. Many of its salts are largely used in the arts. *Acetate of Potash,* which is employed medicinally as a diuretic, is an anhydrous, foliated, very deliquescent, fusible salt, abundantly soluble in alcohol. It combines with a second equivalent of acetic acid when dissolved in the concentrated acid, and forms a crystallizable binacetate, which when subjected to distillation is decomposed into pure monohydrated acetic acid and neutral acetate of potash. *Acetate of Soda* $(NaO, C_4H_3O_3, 6Aq)$ crystallizes in oblique rhombic prisms: it fuses readily. This salt is prepared in large quantities during the purification of wood-vinegar, the crude acid being neutralized sometimes directly by means of carbonate of soda, or soda ash; but in many manufactories, after the crude acid has been neutralized by chalk and thus converted into acetate of lime, the liquid is mixed with sulphate of soda in the proportion of two equivalents of the sulphate to one of the acetate. A soluble acetate of soda is thus obtained by double decomposition, whilst a heavy crystalline double sulphate of lime and soda is formed, which can be more easily freed from the mother liquor than the pasty mass which the simple sulphate of lime would produce. *Acetate of Ammonia* is a very soluble salt, which is frequently used medicinally as a diaphoretic. *Acetate of Baryta* crystallizes below 60° with three equivalents of water, in oblique rhombic prisms; at higher temperatures its crystals assume the form of flattened prisms, and retain only one equivalent of water: it is more soluble in cold than in hot water, and is slightly soluble in alcohol; it is occasionally used as a precipitant for sulphuric acid; when distilled it furnishes acetone. *Acetate of Lime* crystallizes in silky needles, which are pharmacy as *distilled* vinegar. The strength of any vinegar is best ascertained by determining the quantity of anhydrous carbonate of soda which a given weight of it will neutralize: 100 grains of carbonate of soda corresponding to 96·2 grains of the anhydrous acid. Care must be taken to ascertain the absence of sulphuric or of any other acid when operating in this way. Commercial vinegar is allowed by law to contain $\frac{1}{1000}$th of its weight of sulphuric acid; the presence of which prevents the vinegar from becoming mouldy.

Monohydrated acetic acid is best procured in a pure form by distilling acetate of soda with sulphuric acid, diluted with one-fourth of its weight of water. Either binacetate of potash or acetate of copper, when submitted to distillation without any addition, also furnishes the concentrated acid with facility.

(1168) *Properties of Acetic Acid.*—Normal acetic acid ($HO, C_4H_3O_3$ *sp. gr.* 1·063 at 62°) is liquid at temperatures above 55° F., at which temperature it crystallizes in radiating tufts of plates. It may be mingled in all proportions with water, and its density increases on dilution, until it contains three equivalents of water, when its density is 1·079. If it be further diluted, the density diminishes according to the ordinary law. In consequence of this anomaly, monohydrated acetic acid, and the same acid diluted with an equal weight of water, possess each the sp. gr. 1·063. The concentrated acid has a sharp aromatic taste, and a peculiar pungent odour; it blisters the skin if applied to it for a sufficient length of time. It boils at 243°, and may be distilled unchanged. The vapour of this acid is inflammable, producing by its combustion water and carbonic acid. The vapour of acetic acid exhibits an anomalous dilatation when exposed to a gradually rising temperature:—

At 69° the density is	3·95	At 392° the density is	2·22
At 257° „ „ „	3·2	At 446° „ „ „	2·09
At 320° „ „ „	2·48	At 460° „ „ „	2·08;

and beyond this it undergoes no further alteration until the acid is itself decomposed. At 446° and upwards, 1 equivalent of the acid follows the usual law of yielding 4 volumes of vapour (Bineau).

Acetic anhydride ($C_4H_3O_3, C_4H_3O_3$) *Sp. gr. of liquid at 69* 1·073; *of vapour* 3·47.—This compound was obtained by Gerhar
by several methods; but the easiest consists in di
of oxychloride of phosphorus with eight of an
potash, returning the liquid which passes over
and istilling, until the odour of the chloride

exposure to the air these crystals become covered with an efflorescence composed of diacetate of copper. If the acetate be crystallized from an acid solution below 40°, a blue salt is obtained with 5 equivalents of water.

The *diacetate of copper*, or *verdigris* ($2\,CuO, C_4H_3O_3, 6\,Aq$).—For commercial purposes this compound is prepared by exposing sheets of copper piled up, with alternate layers of the fermenting husks of raisins: after a lapse of some weeks the plates of copper become covered with a crust of the salt; this is detached, made into a thick paste with vinegar, and pressed into moulds. The mass thus obtained is of a bluish green colour, it is tough and is reduced to powder with difficulty. In this mode of preparing the salt, the alcohol contained in the grape skins becomes slowly oxidized and converted into acetic acid; the metal also absorbs oxygen gradually from the air; and the oxide thus formed combines with the acetic acid.

Verdigris, when treated with water, is decomposed into an insoluble *tribasic acetate of copper*, and a soluble *subsesquiacetate* ($3CuO, 2C_4H_3O_3, 6Aq$): the latter salt may be obtained in crystals on evaporating the solution.

The *tribasic acetate* is the most stable of the acetates of copper; it assumes the form either of bluish grey needles, or of a green crystalline powder: when heated to 212° it becomes anhydrous.

The neutral acetate of copper unites with the arsenite of this metal, forming *Schweinfurth green*, $CuO, C_4H_3O_3 + 3\,(CuO, AsO_3)$. It may be obtained by mingling boiling solutions of equal weights of arsenious acid and acetate of copper, and adding to the mixture an equal bulk of cold water: if it be allowed to stand for some days a beautiful crystalline green pigment is produced.

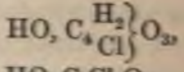
The subacetate of mercury ($Hg_2O, C_4H_3O_3$) is the least soluble of the acetates; it is dissolved readily by boiling water, but it is partially decomposed by ebullition of the solution, and converted into a mixture of metallic mercury and a sparingly soluble basic acetate. The subacetate crystallizes in anhydrous silvery scales, which are quickly blackened by exposure to light.

Acetate of silver is occasionally employed as a reagent; it is sparingly soluble in cold water, but is readily dissolved by hot water, which on cooling deposits it in thin, flexible, anhydrous, silky needles. It is readily obtained by mixing a concentrated solution of nitrate of silver with a solution of acetate of potash, or of soda.

(1169 *bis*) The acetates are distinguished by the pungent odour of acetic acid which they emit when heated with sulphuric acid. When heated with lime they yield acetone (1096), which has a peculiar and characteristic odour; when distilled with hydrate of potash they yield light carburetted hydrogen; and upon this reaction the best method of obtaining marsh gas is founded (401).

Cold solutions of the acetates give with nitrate of suboxide of mercury, a precipitate of the subacetate. Another character is the formation with oxide of lead of a soluble basic salt, with an alkaline reaction.

(1170) *Chlorinated derivatives of acetic acid.*—Acetic acid when acted on by chlorine forms two compounds, in which a portion of its hydrogen is displaced by chlorine, viz.:—

Chloracetic acid	 $HO, C_4\left.\begin{matrix}H_2\\Cl\end{matrix}\right\}O_3,$
Trichloracetic acid	$HO, C_4Cl_3O_3.$

Chloracetic Acid ($HO, C_4H_2ClO_3$) is a colourless liquid which has the odour of acetic acid. In order to obtain it, gaseous chlorine is made to act upon hydrated acetic acid, diluted with half its volume of water; taking care to avoid exposing the mixture to the sun's rays. The gas is transmitted until it ceases to be absorbed, even at a temperature of 212°: the excess of chlorine is then removed by means of a current of carbonic acid gas, whilst the liquid is still maintained at the boiling point. This acid forms definite salts, in which, when dilute, a solution of nitrate of silver occasions no precipitate.

Trichloracetic Acid ($HO, C_4Cl_3O_3$); *Sp. gr. of crystals* 1·617: *of vapour* 5·3.—This acid is usually prepared by exposing glacial acetic acid in large bottles, filled with gaseous chlorine, to the action of the sun: about one drachm of acetic acid should be used for each gallon of chlorine. A complicated reaction ensues, in which, in addition to the trichloracetic acid, oxychloride of carbon, and carbonic and oxalic acids are formed, mixed with an ethereal compound which contains chlorine. The trichloracetic acid is deposited upon the sides of the vessel in white flocculi, which are very deliquescent. It is monobasic, and forms soluble salts, many of which may be obtained in crystals; the chloracetates, when heated, are decomposed into oxychloride of carbon and carbonic oxide, leaving a residue of a metallic chloride. For example:—

$$\overbrace{KO, C_4Cl_3O_3}^{\text{Chloracet. Potash.}} = KCl + 2\,\overbrace{(COCl)}^{\text{Oxychlor. Carbon.}} + \overbrace{2\,CO.}^{\text{Carb. Oxide.}}$$

Trichloracetic acid is also produced by the oxidation of chloral by fuming nitric acid; $C_4HCl_3O_2 + O_2$ becoming $(HO, C_4Cl_3O_3)$, and this is one of the best modes of preparing it, since the excess of nitric acid is easily removed by distillation. After the nitric acid has been expelled, the residue is dissolved in water, and crystallized by spontaneous evaporation over sulphuric acid, *in vacuo.* Chloracetic acid is formed also by the simultaneous action of chlorine and water on protochloride of carbon; $C_4Cl_4 + 4HO + Cl_2 = 3HCl + (HO, C_4Cl_3O_3)$: it may likewise be procured by the decomposition of perchlorinated vinic ethers by water.

The monohydrate of this acid crystallizes in colourless rhombohedra, which are fusible at 115°, and are very deliquescent; the acid has a slight odour, and an acrid sour taste. It bleaches the tongue, and if applied to the skin raises blisters. It boils at about 392°, and may be distilled without decomposition, yielding a suffocating vapour.

Trichloracetic acid, when treated with an amalgam of potassium, yields chloride of potassium, and acetate of potash is reproduced:—

$$\overbrace{HO, C_4Cl_3O_3}^{\text{Trichloracetate of Potash.}} + 6K + 4HO = \overbrace{KO, C_4H_3O_3}^{\text{Acetate of Potash.}} + 3KCl + 2(KO,HO).$$

(1171) *Sulphacetic Acid* $(2HO, C_4H_2S_2O_8) = (C_4H_4O_4, S_2O_6)$.—Acetic acid combines with anhydrous sulphuric acid and forms a dibasic acid, which may be obtained crystallized in deliquescent needles: it forms crystallizable salts. The solution of this acid is not decomposed by ebullition: it gives no precipitate with salts of lead or of lime, but with baryta it forms a crystalline compound of sparing solubility. The sulphacetate of silver crystallizes readily in long flattened prisms.

(1172) *Thiacetic Acid* $(C_4H_4S_2O_2 = HS, C_4H_3O_2S)$.—When monohydrated acetic acid is acted upon by the tersulphide of phosphorus (PS_3), or the pentasulphide (PS_5), a colourless liquid is obtained which has a mingled odour of acetic acid and sulphuretted hydrogen: it boils at about 200°, and is miscible with water in all proportions. It has an acid reaction and a sour taste: when heated upon granulated zinc, the metal is dissolved with evolution of hydrogen; when added to a strong solution of a soluble salt of lead, a sparingly soluble monobasic lead salt is precipitated, which readily undergoes decomposition, even when dry; whilst sulphide of lead is separated. *Thiacetic anhydride* $(C_4H_3O_2S, C_4H_3O_2S)$ is obtained by distilling pentasulphide of phosphorus with acetic anhydride.

It is a colourless oily liquid, which boils at 250°, and emits an odour similar to that of its hydrate. It is heavier than water, which gradually decomposes it into a mixture of hydrated acetic and thiacetic acids. (Kekulé, *Proceed. Roy. Soc.*, vol. vii. p. 37.)

$$\overbrace{(C_4H_3O_2S, C_4H_3O_2S)}^{\text{Thiacetic Anhydride.}} + 2\,HO = \overbrace{(HO, C_4H_3O_3)}^{\text{Acetic Acid.}} + \overbrace{(HS, C_4H_3O_2S)}^{\text{Thiacetic Acid.}}$$

This compound is only one of a series which may be obtained by similar means from other acids homologous with the acetic: thio formic acid (HS, C_2HO_2S) has also been obtained. Thiacetic acid may be regarded as ordinary hydrated acetic acid in which the basic water has been displaced by sulphuretted hydrogen; at the same time one of the equivalents of oxygen in the acid itself has been displaced by an equivalent of sulphur:—

If acetic acid be represented as . . . $\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2$

Thiacetic acid would be . . . . . . $\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}S_2$.

This confirms the view of Gerhardt that the radicle of the volatile fatty acids is to be regarded rather as ($C_nH_{n-1}O_2$) than as (C_nH_{n-1}); the radicle of acetic acid being ($C_4H_3O_2$) instead of (C_4H_3), for hitherto one equivalent only out of the three of oxygen present has been displaced by chlorine, or by sulphur; acetic oxychloride, for example, being $C_4H_3O_2Cl$ (1097).

(1173) FORMIC ACID (HO, C_2HO_3). *Sp. gr. of liquid* 1·2227 *at* 32°; *of vapour* 2·125.—This acid derives its name from the circumstance of its having been first obtained from the *formica rufa*, or red ant, which when irritated ejects an acid liquid: the same acid is excreted by several other insects. It is also found in a free state in the leaves of the stinging-nettle (*urtica urens*). Formic acid, however, derives its importance from the variety of chemical reactions by which it is produced. It is a frequent product of the oxidation of organic bodies; those which belong to the amylaceous group yield it by various processes of oxidation; such as by heating them with hydrate of potash, or with chromic acid, or with a mixture of sulphuric acid and peroxide of manganese. Gelatin and the albuminoid bodies also yield it, mixed with a variety of other products, when they are submitted to the oxidizing influence of chromic acid, or of a mixture of sulphuric acid and black oxide of manganese.

Preparation.—The preparation of formic acid may be effected in the laboratory in several ways.

1. Berthelot has recently succeeded in procuring formic acid by acting upon moist hydrate of potash by means of carbonic oxide; the gas becomes slowly absorbed when exposed in contact with the moistened alkali to a temperature of 212° :—

$$\mathrm{KO, HO} \;+\; 2\,\mathrm{CO} \;=\; \mathrm{KO, C_2HO_3}.$$

Though the quantity of the acid obtained in this remarkable reaction is comparatively small, yet its synthetic production in this manner is a highly interesting circumstance.

2. Oxalic acid, when mixed with an equal bulk of sand and distilled, may also be employed as a source of formic acid, whilst carbonic acid is expelled :—

$$\overbrace{2\,\mathrm{HO, C_4O_6}}^{\text{Oxalic Acid.}} \;=\; \overbrace{\mathrm{HO, C_2HO_3}}^{\text{Formic Acid.}} \;+\; 2\,\mathrm{CO_2}.$$

In the ordinary mode of conducting this operation a large quantity of the formic acid is itself decomposed, owing to the high temperature required to effect the distillation; water and carbonic oxide being the result of its decomposition :—

$$\mathrm{HO, C_2HO_3} \;=\; 2\,\mathrm{HO} \;+\; 2\,\mathrm{CO}.$$

Berthelot has, however, succeeded in rendering this decomposition perfectly manageable in the following manner :—

2 lb. of syrupy glycerin, and 4 or 5 ounces of water, are placed in a retort into which 2 lb. of commercial oxalic acid have been introduced: a receiver is then adapted to the retort and the temperature is gradually raised to 212° or 220°. Brisk effervescence soon ensues owing to the escape of pure carbonic acid: in about fifteen hours the whole of the oxalic acid is decomposed; a small quantity of formic acid will be found condensed in the receiver, but the greater portion remains in the retort. A pint of water is next added to the contents of the retort, and the solution is distilled, adding fresh water as fast as it evaporates. When a gallon and a half or two gallons of water have thus been distilled, the whole of the formic acid will have passed over. The glycerin which remains in the retort may be employed as before to decompose a fresh portion of oxalic acid, and the same series of operations may be repeated with the same quantity of glycerin for an indefinite number of times. Crystallized oxalic acid thus furnishes more than a third of its weight of monohydrated formic acid. This is the best and most productive process at present known for the preparation of formic acid. The principal precaution required is not to allow the temperature to rise too high: if it

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reach 360° or 390° the formic acid itself is decomposed, and an evolution of pure carbonic oxide takes place. This reaction may be taken advantage of in order to obtain pure oxide of carbon by means of oxalic acid. The glycerin acts in some manner unknown in favouring the decomposition of oxalic acid at a lower temperature than would occur if heat alone were employed to effect the metamorphosis: no chemical action, so far as is yet ascertained, takes place between the glycerin and any of the compounds concerned in the reaction (*Ann. de Chimie*, III. xlvi. 484). A solution of mannite acts upon oxalic acid at 212°, in a manner similar to one of glycerin.

3. Formic acid may also be obtained by the oxidation of methylic alcohol under the influence of finely divided platinum:—

$$\overbrace{C_2H_4O_2}^{\text{Wood Spirit.}} \quad + \quad 4\,O \quad = \quad \overbrace{(HO,\,C_2HO_3)}^{\text{Formic Acid.}} \quad + \quad 2\,HO.$$

The oxidation, however, is very liable to proceed too far, water and carbonic acid being formed in large quantity:—

$$HO,\,C_2HO_3 \;+\; 2\,O \;=\; 2\,CO_2 \;+\; 2\,HO.$$

4. The method which has generally been resorted to for the preparation of formic acid, is one discovered by Döbereiner and modified by Liebig. This consists in mixing in a very capacious retort 1 part of starch,* 4 parts of deutoxide of manganese, and 4 of water; 4 parts of sulphuric acid are then added by degrees, when the mixture froths up to 8 or 10 times its bulk, from the abundant extrication of carbonic acid. When this has ceased, distillation is proceeded with, and an impure, dilute formic acid distils over. It is neutralized by carbonate of lead, and the formiate is purified by crystallization. When this salt is distilled with one equivalent of sulphuric acid, the pure monohydrated formic acid passes over.

Properties.—Monohydrated formic acid is a fuming liquid of an irritating odour. It is extremely corrosive, and occasions vesications and painful sores if dropped upon the skin. Below 32 it crystallizes in brilliant scales, and boils at 221°·5, yielding an inflammable vapour which burns with a blue flame. Formic acid yields two definite hydrates with water, $HO,\,C_2HO_3$ and $HO,\,C_2HO_3,\,Aq.$

Gerhardt was unsuccessful in his attempts to procure the anhydride of formic acid.

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* bstances, such as sugar, chaff, bran, sawdust, tart
for starch in this operation with more or

Formiates.—Formic acid is considered to be monobasic, but biformiates of potash and soda may be obtained. All the formiates are soluble. *Formiate of soda* (NaO, C_2HO_3, 2 Aq) assumes the form of rhombic prisms, which are slightly deliquescent. *Formiate of baryta* crystallizes readily in brilliant anhydrous prisms. *Formiate of lead* requires about 40 parts of cold water for solution; but it is freely soluble in hot water, from which it crystallizes in long prismatic anhydrous needles. If a current of sulphuretted hydrogen be passed over this salt, while it is gently heated in a long tube, sulphide of lead is formed, and a monohydrate of the acid is liberated, and may be collected in a suitable receiver. A soluble *tribasic formiate of lead* may also be obtained. *Formiate of copper* (CuO, C_2HO_3, 4 Aq) crystallizes in large blue rhomboidal prisms; it forms double salts with the formiates of baryta and strontia.

Formic acid is easily reconverted into oxalic acid. If a mixture of formiate of soda and hydrate of baryta be heated, hydrogen is evolved, and an oxalate of one of the bases is formed; 2 equivalents of formic acid containing the elements of 1 equivalent of oxalic acid, and 2 equivalents of hydrogen:—

$$\overbrace{2\,(HO, C_2HO_3)}^{\text{Formic Acid.}} \quad = \quad \overbrace{2\,HO, C_4O_6}^{\text{Oxalic Acid.}} \quad + \quad H_2.$$

By a stronger heat the oxalic acid is decomposed, and carbonic acid is formed. Chlorine converts formic acid entirely into hydrochloric and carbonic acids. Nitric acid and other oxidizing agents convert it into carbonic acid and water. Formic acid is a powerful reducing agent, the free acid at a boiling temperature reducing the salts of silver, of mercury, of gold, and of platinum, whilst pure carbonic acid is evolved. Its reducing action upon the compounds of platinum may sometimes serve as an indication of the presence of formic acid in solution. The formiates are decomposed by strong sulphuric acid in excess, pure carbonic oxide and water being the sole products; $HO, C_2HO_3 = 2\,CO + 2\,HO$.

(*b*) *Acids of the Oleic Series*, $HO, (C_nH_{n-3})\,O_3$.

(1174) The acids which belong to this group have been less perfectly studied than those of the foregoing one. Oleic acid is the most important member of this series. Owing to the facility with which these acids absorb oxygen, and the difficulty of purifying them from the results of this oxidation on account of their indisposition to crystallize, the investigation of these compounds is distilled with considerable difficulty. The higher terms of this series are decomposed, when they are heated with a view to effect their distillation.

The acids of this group are characterized by their tendency when gently heated with hydrate of potash, to break up into acetic acid and a second acid of the stearic series, whilst hydrogen is liberated. Oleic acid in this manner yields acetic and palmitic acids:—

$$\underbrace{HO,C_{36}H_{33}O_3}_{\text{Oleic acid.}} + 2(KO,HO) = \underbrace{KO,C_4H_3O_3}_{\text{Acetate of Potash.}} + \underbrace{KO,C_{32}H_{31}O_3}_{\text{Palmitate of Potash.}} + 2H.$$

Acrylic acid when similarly treated yields acetic and formic acids:—

$$\underbrace{HO,C_6H_3O_3}_{\text{Acrylic acid.}} + 2(KO,HO) = \underbrace{KO,C_4H_3O_3}_{\text{Acetate of Potash.}} + \underbrace{KO,C_2HO_3}_{\text{Formiate of Potash.}} + 2H.$$

The acids of this group possess the remarkable property of being converted by peroxide of nitrogen into metameric acids, which require a much higher temperature for their fusion than the oily acids from which they were obtained. These solid acids may be distilled unchanged. When these less fusible metameric acids are heated with hydrate of potash, they also undergo decomposition into acetic acid, and another acid of the stearic series; hydrogen being evolved, exactly as in the case of their more fusible metamerides.

The following table contains the names of the acids of both isomeric series which are at present known. The formulæ of some of the higher terms will probably be modified hereafter, and the number of equivalents of carbon will possibly in all these cases be found to be divisible by four:—

Acids of the Oleic Series ($HO, C_nH_{n-3}O_3$), or ($C_nH_{n-2}O_4$).

Liquid Acids.				Metameric solid Acids.			
		Fusing point.	Origin.			Fusing point.	Origin.
Erucic -	$C_{44}H_{42}O_4$	95°	Mustard seed and rapeseed.				
Doeglic -	$C_{38}H_{36}O_4$	64°	The Dögling whale.				
Oleic - -	$C_{36}H_{34}O_4$	57°	Non-drying oils.	Elaidic	$C_{36}H_{34}O_4$	113°	Action of (NO_4) on oleic acid.
Physetoleic	$C_{32}H_{30}O_4$		Sperm whale.				
Moringic -	$C_{30}H_{28}O_4$	32°	Oil of Ben.	Angelic	$C_{10}H_8O_4$	113°	Angelica root.
Acrylic -	$C_6H_4O_4$		Distillation of glycerin.				

(1175) It will not be necessary to describe any of these acids in detail except the oleic :—

1. *Erucic acid* is extracted from the oil of the white and black mustard seed, and from colza oil. It is liquid at temperatures above 93°.

2. *Doeglic acid* is extracted by Scharling from the oil of the *Balæna rostrata* (in Danish, *Dögling*), a species of sperm whale. The composition of this oil is remarkable, since it does not furnish glycerin when saponified, but a compound, $HO, C_{24}H_{25}O$, which corresponds in composition to lauric alcohol. The oil when distilled gives no acrolein, showing the absence of glycerin.

3. *Physetoleic acid* was obtained from the oil of the ordinary sperm whale (*Physeter macrocephalus*).

4. *Moringic acid* is the liquid acid extracted from the oil of ben (*Moringa aptera*); it becomes solid at 32°. Oil of ben, from its indisposition to become rancid, has been used as the basis of Macassar oil.

5. *Angelic acid* ($HO, C_{10}H_7O_3$) is met with in the root of various kinds of angelica; it is also produced by the action of hydrate of potash, aided by a gentle heat, upon the oxidized principle in the essence of camomile :—

$$\overbrace{C_{10}H_8O_2}^{\text{Ess. Camomile.}} + KO, HO = \overbrace{KO, C_{10}H_7O_3}^{\text{Angelate of Potash.}} + 2\,H.$$

This acid forms large, striated, colourless prisms, which fuse at 113°; it boils at 374°, and may be distilled without undergoing decomposition. It is sparingly soluble in cold water, but freely so in boiling water. When heated with hydrate of potash, it is decomposed with escape of hydrogen into acetate and propionate of potash, in accordance with the general mode of decomposition of the oleic series. From its high fusing point, and from the possibility of distilling it without decomposition, it is, however, obvious that it does not belong to the oleic series, but probably to the elaidic group.

6. *Acrylic acid* ($HO, C_6H_3O_3$) is obtained by the oxidation of acrolein. This is best effected by digesting acrolein on oxide of silver in excess; the pungent smell of acrolein disappears, and acrylate of silver is obtained in solution, whilst metallic silver is deposited, and water is eliminated :—

$$\overbrace{C_6H_3O, HO}^{\text{Acrolein.}} + 3\,AgO = \overbrace{AgO, C_6H_3O_3}^{\text{Acrylate of Silver.}} + 2\,Ag + HO.$$

If the acrylate of silver be placed in a bulb tube, kept cool by immersion in ice, it may be decomposed by transmitting over it a very slow current of sulphuretted hydrogen; sulphide of silver is formed, whilst hydrated acrylic acid is liberated; the latter may be distilled by a gentle heat. Acrylic acid has an agreeable acid odour and a burning taste. It requires a temperature below 32° to freeze it. Its boiling point is above 212°, and it may be distilled unchanged. All its salts are soluble: the salt of silver is one of the most characteristic compounds of this acid; it crystallizes in anhydrous silken needles, which much resemble the acetate of silver in appearance; it is sparingly soluble in cold water: boiling water decomposes it, and partially reduces the silver. Acrylate of silver may readily be formed from the crude products of the distillation of oils; the distillate is rectified, and those portions which come over between 100° and 140° are collected separately; they are rectified anew from chloride of calcium, and are then digested on an excess of oxide of silver, returning the portions which distil, until the pungent odour of acrolein has disappeared: water is next added, and the liquid is distilled to carry off the volatile oils; after which the boiling liquid is filtered and set aside in a dark place to crystallize. *Acrylate of soda* crystallizes with 5 Aq in efflorescent prisms which are very soluble. *Acrylate of baryta* does not crystallize.

(1176) OLEIC ACID ($HO, C_{36}H_{33}O_3$).—The isolation of this acid in a state of purity is a matter of some difficulty, owing to its tendency to combine with oxygen. Oleic acid is obtained in a crude form as a secondary product in the manufacture of stearin candles. In order to obtain the pure acid, Varrentrapp recommends that almond oil be saponified with potash or with soda, and that the soap be decomposed with hydrochloric acid. The mixed fatty acids are then to be digested with half their weight of finely powdered oxide of lead. On digesting the mixed salts of lead with twice their volume of ether for 24 hours, the oleate of lead is dissolved and separated from the other salts. The ethereal solution is then to be mixed with dilute hydrochloric acid, which decomposes the oleate; the oily acid is dissolved by the ether and rises to the surface. The ether is to be expelled by heat, and the acid is again to be converted into soap by the addition of an alkali; after which it is separated from its aqueous solution by the addition of chloride of sodium, pressed, redissolved in water which has been boiled for some time to expel the air, and finally decomposed by tartaric acid in vessels filled with carbonic acid gas. The acid thus obtained always has a brown colour, owing to the action of atmospheric oxygen upon it. Gottlieb purified it by adding to the acid thus obtained a large excess of ammonia, and then precipitating it by means of chloride of barium: the oleate of baryta thus procured is dried and boiled with alcohol. During this operation the salt melts and forms a viscous liquid, but a portion of it is dissolved and is deposited in crystalline plates as the liquid cools; these are again crystallized from alcohol, and on decomposing them with tartaric acid pure oleic acid is obtained. The alcohol in the preceding operation retains the impurities which render the ordinary oleate of baryta so fusible: pure oleate of baryta is not fusible at 212°.

Pure oleic acid, at temperatures above 57°, forms a colourless, limpid oil, without taste or smell; it does not redden litmus even when dissolved in alcohol; at 40° it concretes into a hard crystalline mass, composed of fine needles. When solid it undergoes no change in the air, but when liquid it absorbs oxygen rapidly, acquiring a brown colour, a rancid odour, and an acid reaction upon litmus, its point of solidification gradually becoming lowered until it falls below 0·° F. Oleic acid cannot be distilled without undergoing decomposition: a large quantity of liquid and of gaseous hydrocarbons are given off in the distillation, besides several acids of the series $C_nH_nO_4$, but the most characteristic product is sebacic acid (1179), the quantity of which, however, appears to diminish in proportion as the oleic acid has become more oxidized.

Oleic acid forms two classes of salts, neutral and acid. The neutral salts of the alkalies are the only soluble ones. They form soaps, and by the evaporation of their aqueous solution they may be obtained in the condition of an amorphous mass. Oleate of potash forms a soft soap, which is the chief ingredient in Naples soap. Oleate of soda is a hard soap, and enters largely into the composition of Marseilles soap. The acid oleates of the alkalies are liquid and insoluble. The metallic oleates, such as those of copper and lead, are soluble in cold anhydrous alcohol and in ether; they are thus separable from the stearates and palmitates, which are insoluble in these liquids.

(1177) *Action of Peroxide of Nitrogen and of Nitric Acid on Oleic Acid.*—Oleic acid by exposure to peroxide of nitrogen becomes converted into a solid fatty acid, isomeric with oleic acid, which has been called *elaidic acid.* In effecting this change an excess of the peroxide must be avoided, and the mass must be kept cool. The cause of this remarkable change is unknown. A small quantity of ammonia is formed during the reaction, as well as a portion of a neutral oily body. The quantity of peroxide of nitrogen required is very small, not exceeding $\frac{1}{200}$th of the weight of the oleic acid.

Elaidic acid fuses at about 113°; it is very soluble in alcohol, from which it is deposited in beautiful pearly scales; it is less soluble in ether. Elaidic acid may be distilled in great part without alteration; but when fused with hydrate of potash it yields palmitic and acetic acid, like oleic acid.

When oleic acid is subjected in a capacious retort to the action of a large excess of nitric acid of sp. gr. 1·42 diluted with an equal bulk of water, it gradually disappears, producing a copious evolution of nitrous fumes, attended with a violent reaction. The results of the decomposition are very complicated, but the products obtained by this method of oxidizing oleic acid present considerable interest, since they contain, according to Redtenbacher, all the terms of the homologous series of the volatile acids ($C_nH_nO_4$) from the acetic to the capric acid inclusive, these acids being found in the distillate; whilst according to Laurent (*Ann. de Chimie*, II. lxvi. 154), four fixed acids are left in the retort, and these form contiguous terms of a group of homologous dibasic acids of the formula $2\ HO, (C_nH_{n-4})\ O_6$. The quantity of the volatile acids is greater when the nitric acid used is very concentrated; if it be more dilute, that of the fixed acids is increased. The fixed acids which remain in the retort, are the following:—

Suberic acid	$2\ HO, C_{16}H_{12}O_6$
Pimelic acid	$2\ HO, C_{14}H_{10}O_6$
Adipic acid	$2\ HO, C_{12}H_8\ O_6$
Lipic acid	$2\ HO, C_{10}H_6\ O_6$?

It is interesting to remark that another acid of this group—viz., the sebacic acid ($2\ HO, C_{20}H_{16}O_6$) is a characteristic product of the distillation of oleic acid; and succinic acid ($2\ HO, C_8H_4O_6$), which is one of the most frequent products of the action of nitric acid upon the series of acids ($C_nH_nO_4$) is the next term below the lipic acid. Some of the acids of this series will now be described.

(c) *Dibasic Acids of the Oxalic Series* ($2\ HO, C_nH_{n-4}O_6$).

(1178) All the acids belonging to this series possess a considerable volatility, and may be partially sublimed without undergoing decomposition: they are soluble to a large extent in boiling water as well as in alcohol: they are likewise soluble in ether, and may be obtained in crystals without difficulty. Gerhardt proposes to double the formula for oxalic acid, and to consider it as dibasic, as it possesses all the properties of this class of compounds. It would then form the lowest term in this group. The following table contains the names of the acids which have been ascertained to belong to this series:—

Acids.	Formulæ.	Fusing point.	Appearance.
Sebacic . .	$2\,HO, C_{20}H_{16}O_6$	260°	Thin pearly plates.
Suberic . .	$2\,HO, C_{16}H_{12}O_6$	257°	White crystalline powder.
Pimelic . .	$2\,HO, C_{14}H_{10}O_6$	237°	Hard granular crystals.
Adipic . .	$2\,HO, C_{12}H_8\,O_6$	266°	Radiated tufts.
Lipic ? . . .	$2\,HO, C_{10}H_6\,O_6$	about 290°	Long plates, very soluble.
Succinic . .	$2\,HO, C_8\,H_4\,O_6$	356°	Four-sided prisms.
Oxalic . . .	$2\,HO, C_4\qquad O_6$	Sublimes before fusing.	4-sided prisms with 4 Aq.

(1179) *Sebacic Acid* ($2\,HO, C_{20}H_{16}O_6$).—This acid is easily obtained by the distillation of oleic acid, and most of the fixed oils also yield it by distillation, owing to the decomposition of the olein which they contain: the acid is accompanied in this operation by various hydrocarbons, and by other volatile acids. It may likewise be readily obtained in large quantity from the fixed residue of the distillation of castor oil with hydrate of potash; ricinolic acid yielding octylic (caprylic) alcohol, sebacic acid, and free hydrogen:—

$$\overbrace{HO, C_{36}H_{33}O_5}^{\text{Ricinolic Acid.}} + 2(KO, HO) = \overbrace{C_{16}H_{17}O, HO}^{\text{Octylic Alcohol.}} + 2\,\overbrace{KO, C_{20}H_{16}O_6}^{\text{Sebate of Potash.}} + 2\,H.$$

The sebate of potash is dissolved in boiling water and decomposed by the addition of hydrochloric acid; sebacic acid crystallizes in needles as the liquid cools. This acid is readily recognised by its ready solubility in boiling water, from which it crystallizes in pearly scales, as it is nearly insoluble at ordinary temperatures. It fuses at 260°, and may be sublimed without decomposition, becoming condensed in needles which resemble those of benzoic acid. Its vapours have a greasy odour, and produce a very irritating effect upon the lungs. Sebacic acid is very soluble in alcohol and in ether.

Sebacic acid forms both acid and neutral salts. The sebates of the alkalies and of the earths are soluble, but the other sebates are nearly insoluble. The acid ($2\,HO, C_{18}H_{14}O_6$) intermediate between the sebacic and suberic in this series is not known.

(1180) *Suberic Acid* ($2\,HO, C_{16}H_{12}O_6$).—This compound was originally observed among the products of the oxidation of cork by nitric acid, and hence it derives its name (from *suber*, cork).

Cork, however, yields it in but very small quantity, and even that quantity is probably owing to the presence of a small proportion of waxy matter. The acid is rather a frequent product of the oxidation of the fats, and particularly of the stearic acid series. It is easily obtained by boiling stearic acid with nitric acid for some days; upon concentrating the liquid it deposits crystals of suberic acid, mixed with a large quantity of succinic acid. The latter acid is easily removed by washing with cold water, and the sparingly soluble suberic acid is purified by crystallization from boiling water. It forms a white crystalline powder, destitute of odour, but having a slight acid taste, and feebly reddening litmus paper. It requires about 100 times its weight of cold water for solution, but only twice its weight of boiling water. It is also soluble in alcohol and in ether. When heated it fuses at about 257°, and creeps up the side of the vessel in which it is heated; undergoing a sort of spurious sublimation at a high temperature. The suberates of the alkalies and of the earths are soluble and crystallizable; they yield with salts of lead, silver, and zinc, white sparingly soluble precipitates.

The three next terms of the series—viz., the pimelic, adipic, and lipic acids, are unimportant: they are formed along with suberic acid during the oxidation of oleic by nitric acid; these acids may be crystallized without difficulty.

(1181) *Succinic Acid* ($2\,HO, C_8H_4O_6$).—This acid, as its name implies, was originally obtained from amber (*succinum*), in which it exists ready formed. When amber is submitted to destructive distillation, a quantity of succinic acid passes over amongst other substances. It is, however, easily obtained artificially by acting upon stearic or palmitic acid with nitric acid. Succinic acid also occurs in the leaves of the wormwood and in the resins of many of the pine tribe. It may likewise be obtained, by fermentation, from asparagin, and from malic acid (Dessaignes), malate of lime yielding nearly one-third of its weight of it. In order to procure it from malic acid 3 lb. of crude malate of lime are to be diffused through a gallon of warm water, and four ounces of decayed cheese are to be added to the mixture, which is to be kept at a temperature of 100° for about a week. Carbonic acid is disengaged, whilst a mixture of crystallized carbonate and succinate of lime is deposited, and acetate of lime remains in solution (1112).

$$3\overbrace{(2\,CaO, C_8H_4O_8)}^{\text{Malate of Lime.}} = 2\overbrace{(2\,CaO, C_8H_4O_6)}^{\text{Succinate of Lime.}} + \overbrace{CaO, C_4H_3O_3}^{\text{Acetate of Lime.}} + CaO, CO_2 + 3\,CO_2 + HO,$$

The deposited succinate of lime is to be collected upon a linen filter and washed with cold water, after which it may be decomposed by hydrochloric acid, and the succinic acid purified by crystallization. The decomposition, however, is not always so simple as is represented in the foregoing equation. The formation of lactate of lime has often been observed to accompany the transformation of malic into succinic acid, and it frequently happens that a quantity of hydrogen is disengaged during the fermentation : when this occurs it indicates the formation of butyric acid, which is also accompanied by a small quantity of an essential oil with an agreeable odour of apples. The relation of malic to lactic acid is very simple :—

$$2\overbrace{(2\,HO, C_8H_4O_8)}^{\text{Malic Acid.}} = 2\,\overbrace{HO, C_{12}H_{10}O_{10}}^{\text{Lactic Acid.}} + 4\,CO_2\,;$$

and the presence of lactic acid readily accounts for the formation of butyric acid (1164). An interesting relation also exists between butyric and succinic acids; butyric acid when treated with nitric acid being convertible by oxidation into the succinic :—

$$\overbrace{HO, C_8H_7O_3}^{\text{Butyric Acid.}} + 6\,O = 2\,\overbrace{HO, C_8H_4O_6}^{\text{Succinic Acid.}} + 2\,HO.$$

Succinic acid crystallizes in large, regular rhombic tables which require five parts of cold and two of boiling water for solution. Alcohol dissolves it freely, but it is only sparingly soluble in ether. Succinic acid melts at a temperature of from 347° to 356°, but if suddenly heated to 455° it melts, boils, and sublimes completely. During the sublimation the acid loses a portion of its water, and if distilled with anhydrous phosphoric acid the anhydride may be obtained without difficulty ($C_8H_4O_6$). Succinic anhydride is soluble in alcohol and in water; its aqueous solution rapidly becomes converted into the ordinary hydrated acid.

Succinic acid is a very stable compound. It may be boiled for many hours with strong nitric acid without undergoing decomposition, and its aqueous solution is not affected by chlorine, or by a mixture of chlorate of potash and hydrochloric acid. Succinic acid forms three salts with *potash* :—a neutral deliquescent salt ($2\,KO, C_8H_4O_6, 4\,Aq$) ; an acid salt ($KO, HO, C_8H_4O_6, 4\,Aq$; Döpping), which crystallizes in transparent efflorescent six-sided prisms, which are soluble in alcohol; and a remarkable superacid salt [$KO, 2\,HO, 2\,(C_8H_4O_6)\;3\,Aq$], which may also be obtained free from its 3 equivalents of water of crystallization, by raising its temperature to 212° (Fehling). *Succinate of ammonia* ($2\ H_4NO,\ C_8H_4O_6$) is sometimes employed to separate iron in perfectly neutral solutions from salts of nickel, cobalt, and manganese. A double *succinate of magnesia and potash* ($MgO,\ KO,\ C_8H_4O_6,\ 5\ Aq$) may be obtained in double six-sided pyramids, by allowing the two salts mixed in equivalent proportions to crystallize together. Succinic acid forms several nearly insoluble compounds with oxide of *lead;* the neutral compound is white and crystalline $2\ PbO,\ C_8H_4O_6$; another compound, $3\ PbO,\ C_8H_4O_6$, is fusible in warm water; and if either of the foregoing be digested with ammonia, a compound may be obtained with a still larger proportion of base.

The succinates are characterized by the bulky brown precipitates of persuccinate of iron, which they yield in neutral solutions of salts of the sesquioxide of iron.

Succinic acid combines readily with anhydrous sulphuric acid, and forms a deliquescent crystallizable compound acid, termed *sulpho-succinic acid* ($3\ HO,\ C_8H_3O_5,\ 2\ SO_3,\ 2\ Aq$), which requires 3 equivalents of base for its saturation.

(1182) When anhydrous succinic acid is distilled with an equivalent quantity of perchloride of phosphorus, oxychloride of phosphorus passes over at first; and at a more elevated temperature *succinic oxychloride* ($C_8H_4O_4Cl_2$) is obtained. This compound forms a colourless oil of high refracting power, and sp. gr. 1·39: it boils at about 374°, emitting a dense suffocating vapour, which in a very dilute form has an odour of wet straw. A damp atmosphere slowly converts it into crystallized succinic acid. It derives its principal importance from its affording an illustration of the characters and mode of preparation of an oxychloride of a dibasic acid :—

$$\overbrace{C_8H_4O_6}^{\text{Succinic Anhydride.}} + PCl_5 = \overbrace{C_8H_4O_4Cl_2}^{\text{Succinic Oxychloride.}} + PO_2Cl_3.$$

The acid which would have the composition $2HO,\ C_6H_2O_6$, intermediate between the succinic and the oxalic is as yet unknown.

§ IV. GENERAL REVIEW OF THE ALCOHOLS—AROMATIC ALCOHOLS—POLYATOMIC ALCOHOLS.

(1183) *General Summary of the Alcohol Groups.*—Having now completed the description of the more important bodies connected with the series of alcohol and its homologous compounds, it may be serviceable to take a general review of the connexion of these different compounds with each other. For this purpose the following table has been constructed; it furnishes a synoptic view of the more important classes of heterologous derivatives from the alcohols. If space allowed us to map out the whole of the various derivatives of each alcohol in a table similar in principle to that given at pages 32 and 33, each of the general formulæ given in the second column of the present table would stand at the head of one of the columns of such a table. Each substance enumerated in this table is, therefore, to be regarded as the representative of a homologous series of compounds like that of the fatty acids, or of the alcohols, in which each of the members differs from those which precede and follow it by (C_2H_2).

It will be observed that the letters $\overline{W}$, $\overline{X}$, $\overline{Y}$, and $\overline{Z}$, are occasionally employed in the column headed "General formulæ":—

$\overline{W}$ indicates chlorine, or one of the halogens.
$\overline{X}$ indicates an anhydrous monobasic acid.
$\overline{Y}$ indicates an anhydrous dibasic acid.
$\overline{Z}$ indicates an anhydrous tribasic acid.

n and *m* are in all cases supposed to be even numbers. It must be remembered that this table, extensive as it is, does not specify all the known heterologous derivatives of any single alcohol. The different forms of the phosphorus bases are not mentioned, because they are represented by the formulæ of those of ammonium, from which they differ in containing an equivalent of phosphorus in the place of one of nitrogen. Of the homologues of urea two distinct series are known, the first of which

corresponds to ethyl-urea . . $H_3(C_4H_5)\ N_2C_2O_2$
and the second to diethyl-urea $H_2(C_4H_5)_2N_2C_2O_2$

though the former series only is indicated in the table. The zinc radicle again represents other metallic compounds, such as those containing cadmium, which are formed upon the same type. The various arsenio-compounds are also representatives of the antimony series, which are not mentioned in the table; the arsenical compounds likewise are representatives of the compounds which contain bismuth in the place of arsenic. Again, the stanno-radicles, themselves a numerous group, are only indicated by a single formula; whilst the compounds of lead and of mercury correspond to one or other of the different forms of the stanno-radicle.

Heterologous Series derived from the Alcohols.

	Name of the Series and	General Formula.	Examples.	
1.	Electro-positive radicle	$2(C_nH_{n+1})$	Ethyl	$2(C_4H_5)$
2.	Double radicle . . .	(C_nH_{n+1},C_mH_{m+1})	Ethyl-tetryl . .	C_4H_5,C_8H_9
3.	Alcohol	$(C_nH_{n+1},H)O_2$	Alcohol	C_4H_5,H,O_2
4.	Simple ether . . .	$2(C_nH_{n+1})O_2$	Ethylic ether . .	C_4H_5,C_4H_5,O_2
5.	Double ether . . .	$(C_nH_{n+1},C_mH_{m+1})O_2$	Ethyl-amylic ether	$C_4H_5,C_{10}H_{11}O_2$
6.	Hydracid ether . .	$(C_nH_{n+1})\ \overline{W}$	Hydrochloric ether	C_4H_5,Cl
7.	Sulphuretted ether .	$2(C_nH_{n+1})\ S_2$	Hydrosulphuric ether . . .	C_4H_5,C_4H_5,S_2
8.	Bisulphuretted ether .	$2(C_nH_{n+1})\ S_4$	Bisulphide of ethyl	C_4H_5,C_4H_5,S_4
9.	Mercaptan	$(C_nH_{n+1}H)\ S_2$	Ethyl-mercaptan .	C_4H_5,H,S_2
10.	Compound ether (monobasic) . . .	$(C_nH_{n+1})O,\ \overline{X}$	Acetic ether . .	$C_4H_5O,C_4H_3O_3$
11.	Compound ether (dibasic)	$2(C_nH_{n+1})O_2,\overline{Y}$	Oxalic ether . .	$2(C_4H_5)O_2,C_4O_6$
12.	Vinic acid	$HO,(C_nH_{n+1})O,\ \overline{Y}$	Sulphethylic acid .	HO,C_4H_5O,S_2O_6
13.	Salt of vinic acid . .	$MO,(C_nH_{n+1})O,\ \overline{Y}$	Sulphethylate of potash . . .	KO,C_4H_5O,S_2O_6
14.	Compound ether (tribasic)	$3(C_nH_{n+1})O_3,\overline{Z}$	Citric ether . . .	$3(C_4H_5)O_3,C_{12}H_5O_{11}$
15.	Cyanide, or nitrile . .	$C_nH_{n+1})\ Cy$	Hydrocyanic ether (propio-nitrile)	C_4H_5,Cy or C_6H_5N
16.	Amide bases . . .	$H_2(C_nH_{n+1})\ N$	Ethylia	H_2,C_4H_5,N
17.	Imide bases	$H,\ 2(C_nH_{n+1})\ N$	Diethylia . . .	$H,2(C_4H_5)N$
18.	Nitrile bases . . .	$3(C_nH_{n+1})\ N$	Triethylia . . .	$3(C_4H_5)N$
19.	Oxide of ammonium base (hydrated) .	$4(C_nH_{n+1})NO,HO$	Oxide of Tetrethylium (hydrated)	$4(C_4H_5)NO,HO$
20.	Homologues of urea .	$H_3,\ (C_nH_{n+1})N_2C_2O_2$	Ethyl-urea . . .	$H_3,(C_4H_5)N_2C_2O_2$
21.	Zinc-radicle	$Zn\,(C_nH_{n+1})$	Zinc-ethyl . . .	$Zn\,(C_4H_5)$
22.	Diarsenio-radicle . .	$As\ 2(C_nH_{n+1})$	Kakodyl . . .	$As,2(C_2H_3)$
23.	Oxide of diarsenio-radicle . . .	$As\ 2(C_nH_{n+1})O$	Oxide of kakodyl	$As,2(C_2H_3)O$
24.	Acid of diarsenio-radicle. . . .	$HO,As\ 2(C_nH_{n+1})O_3$	Kakodylic acid .	$HO,As\ 2(C_2H_3)O_3$
25.	Triarsenio-Radicle . .	$As\ 3(C_nH_{n+1})$	Triarsenethyl . .	$As\ 3(C_4H_5)$
26.	Oxide of triarsenio-radicle. . . .	$As\ 3(C_nH_{n+1})O_2$	Oxide of triarsen-ethyl . . .	$As\ 3(C_4H_5)O_2$
27.	Hydrated oxide of tetrarsenio-radicle .	$As\ 4(C_nH_{n+1})O,HO$	Hydrated oxide of tetrarsenethylium	$As\ 4(C_4H_5)O,HO$
28.	Stanno-radicles . . .	$X Sn\,x(C_nH_{n+1})$	Bistannethyl . .	$2Sn,\ 2(C_4H_5)$
29.	Homologues of marsh gas	$(C_nH_{n+1})H$	Hydride of ethyl	C_4H_5,H
30.	Homologues of olefiant gas. . . .	$(C_nH_{n-1})H$	Olefiant gas . .	C_4H_3,H
31.	Aldehyds	$(C_nH_{n-1})H,O_2$	Acetic aldehyd . .	C_4H_3,H,O_2
32.	Volatile Acids . . .	$HO,(C_nH_{n-1})O_3$	Acetic acid. . .	$HO,C_4H_3O_3$
33.	Ketones	$C_nH_nO_2$	Acetone	$C_6H_6O_2$
34.	Dibasic acids . . .	$2HO,(C_nH_{n-4})O_6$	Succinic acid . .	$2HO,C_8H_4O_6$
35.	Monobasic anhydrides .	$2(C_nH_{n-1}O_3)$	Acetic anhydride .	$C_4H_3O_3,C_4H_3O_3$
36.	Compound anhydrides	$C_nH_{n-1}O_3,C_mH_{p-1}O_3$	Benzo-acetic do. .	$C_4H_3O_3,C_{14}H_5O_3$
37.	Dibasic anhydrides . .	$C_nH_{n-4}O_6$	Succinic anhydride	$C_8H_4O_6$
38.	Monobasic oxychlorides	$C_nH_{n-1}O_2Cl$	Acetic oxychloride	$C_4H_3O_2Cl$
39.	Dibasic oxychlorides .	$C_nH_{n-4}O_4Cl_2$	Succinic oxychloride . . .	$C_8H_4O_4Cl_2$
40.	Base with electro-negative radicle . .	$H_2(C_nH_{p-1})N$	Acetylia	H_2,C_4H_3,N
41.	Hydrated oxide of ammonium base of electro-negative radicle	$H_3(C_nH_{n-1})NO,HO$	Hydrated oxide of acetylium . .	$H_3(C_4H_3)NO,HO$

(1184) *Groups Isologous with the Alcohols and their Derivatives.*—The progress of research into the products of the decomposition of organic compounds, is gradually disclosing the existence of a number of groups which bear a close relationship to that of the alcohols, already examined : this relationship, however, is not one of homology; for if the new alcohols were homologous with those previously known, they would themselves be members of the group to which these bodies belong.

The groups of which we are now speaking are *isologous* with the alcohols—that is to say, that the compounds which constitute each of these groups are related to each other in a manner similar to that of the components of the alcohol group with which they are compared. For example, a class of compounds is known to the chemist, derived from oil of garlic, and constituting what has been termed the *allylic* series. Another class, related to the fragrant acid contained in gum benzoin, is known as the *benzoic* series; and a third class related to oil of cinnamon, has been termed the *cinnamic* series. Now, upon comparing together the relations of the different heterologous compounds composing each of these three groups, it has been found that certain of them bear to each other, relations similar to those observed between the heterologous compounds derived from alcohol :—For example, in each of the groups just mentioned there is a compound indicated as the *alcohol* of the series : there is another which contains two equivalents of hydrogen less than this body ; it has the power of forming a crystalline compound with bisulphite of potash, and corresponds in properties with the *aldehyds.* It has further been observed that these new aldehyds by combining with two additional equivalents of oxygen furnish *volatile acids,* the normal hydrates of which contain four equivalents of oxygen, and correspond to the series of volatile fatty acids. The alcohols of these three groups are not homologous with ethylic alcohol; for the semi-molecule of *allyl* (the hydrocarbon of the allylic series, corresponding to ethyl), contains one equivalent of hydrogen less than the number of equivalents of carbon, whereas the semi-molecule of ethyl contains one equivalent of hydrogen more than the number of equivalents of carbon. The semi-molecule of the hydrocarbon of the benzoic series, contains seven equivalents of hydrogen less than the number of equivalents of carbon; and in the cinnamic hydrocarbon the disproportion is still greater, the number of equivalents of hydrogen falling short by nine, of that of the proportion of carbon. Yet, all these bodies in their derivatives present an analogy with the corresponding derivatives of alcohol. The allylic, the benzoic, and the cinnamic series, are *isologous* with that of alcohol.

In the benzoic series the existence of three homologous terms is already indicated more or less fully, namely the benzoic, the toluic, and the cuminic series. In the allylic and cinnamic group only a single series is in each case as yet known; but it can scarcely be doubted that other homologous series of each of these varieties of alcohols will be found.

The following table will serve to elucidate the general relations of these groups to each other; and it will also indicate the analogy of the compounds which they form with corresponding compounds in the comprehensive family to which ethylic alcohol belongs :—

ISOLOGOUS GROUPS.

Hydrocarbon.	Oxide.	Chloride.	Alcohol.	Aldehyd.	Volatile Acid.
(1) *Compounds of the Ethylic Series.*					
$2(C_nH_{n+1})$	$2(C_nH_{n+1})O_2$	$(C_nH_{n+1})Cl$	$C_nH_{n+1}O,HO$	$C_nH_{n-1}O,HO$, or $(C_nH_{n-1}O_2,H)$	$HO,C_nH_{n-1}O_3$
$\overbrace{2(C_4H_5)}^{\text{Ethyl.}}$	$\overbrace{2(C_4H_5)O_2}^{\text{Ether.}}$	$\overbrace{C_4H_5Cl}^{\text{Hydrochlor. Ether.}}$	$\overbrace{C_4H_5O,HO}^{\text{Alcohol.}}$	$\overbrace{C_4H_3O_2,H}^{\text{Acetic Aldehyd.}}$	$\overbrace{HO,C_4H_3O_3}^{\text{Acetic Acid.}}$
(2) *Compounds of the Allylic Series.*					
$2(C_nH_{n-1})$	$2(C_nH_{n-1})O_2$	$C_nH_{n-1}Cl$	$C_nH_{n-1}O,HO$	$C_nH_{n-3}O_2,H$	$HO,C_nH_{n-3}O_3$
$\overbrace{2(C_6H_5)}^{\text{Allyl.}}$	$\overbrace{2(C_6H_5)O_2}^{\text{Oxide of Allyl.}}$	$\overbrace{C_6H_5Cl}^{\text{Chloride of Allyl.}}$	$\overbrace{C_6H_5O,HO}^{\text{Allylic Alcohol.}}$	$\overbrace{C_6H_3O_2,H}^{\text{Acrolein.}}$	$\overbrace{HO,C_6H_3O_3}^{\text{Acrylic Acid.}}$
(3) *Compounds of the Benzoic Series.*					
$2(C_nH_{n-7})$	$2(C_nH_{n-7})O_2$	$C_nH_{n-7}Cl$	$C_nH_{n-7}O,HO$	$C_nH_{n-9}O_2,H$	$HO,C_nH_{n-9}O_3$
(1)		$\overbrace{C_{14}H_7Cl}^{\text{Chloride of Benzoene.}}$	$\overbrace{C_{14}H_7O,HO}^{\text{Benzoic Alcohol.}}$	$\overbrace{C_{14}H_5O_2,H}^{\text{Oil of Bitter Almonds.}}$	$\overbrace{HO,C_{14}H_5O_3}^{\text{Benzoic Acid.}}$
(2)					$\overbrace{HO,C_{16}H_7O_3}^{\text{Toluic Acid.}}$
(4)			$\overbrace{C_{20}H_{12}O,HO}^{\text{Cuminic Alcohol.}}$	$\overbrace{C_{20}H_{11}O_2,H}^{\text{Oil of Cummin.}}$	$\overbrace{HO,C_{20}H_{11}O_3}^{\text{Cuminic Acid.}}$
(4) *Compounds of the Cinnamic Series.*					
			$C_nH_{n-9}O,HO$	$C_nH_{n-11}O_2,H$	$HO,C_nH_{n-11}O_3$
			$\overbrace{C_{18}H_9O,HO}^{\text{Styrone.}}$	$\overbrace{C_{18}H_7O_2, H}^{\text{Oil of Cinnamon.}}$	$\overbrace{HO, C_{18}H_7O_3}^{\text{Cinnamic Acid.}}$

Each of these groups contains a well-known essential oil. We shall therefore postpone the consideration of the other derivatives of these various alcohols, until the general properties of the essences come to be considered.

The following chapter will be devoted to the description of the more important essences, as well as of their most interesting derivatives. Before passing to the consideration of these bodies it will, however, be necessary to allude to another class of alcohols, which may be termed polybasic or *polyatomic* alcohols.

(1184 *bis*) *Polyatomic Alcohols.*—In describing the properties and derivatives of glycerin (1147 *et seq.*), allusion has already been made to the existence of other bodies which possess the properties of alcohols, but which combine with more than one equivalent of acid, the neutral fats being substances which may be regarded as the ethers of a *teratomic* alcohol, glycerin. Wurtz (*Comptes Rendus*, July, 1856) has recently discovered a new body, which he terms *glycol*, intermediate in properties between glycerin and alcohol, and which possesses the properties of a *biatomic* alcohol. This substance is derived indirectly from olefiant gas; and there can be no question that the hydrocarbons homologous with olefiant gas will, before long, assume a much more important position in the theory of organic chemistry than has hitherto been assigned to them.

A paper by Mr. Buff, communicated to the Royal Society by Dr. Hofmann (*Proceedings Roy. Soc.*, viii. 188), contains some important observations on the derivatives of olefiant gas. There are, it must be remarked, two classes of hydrocarbons which yield uniatomic alcohol radicles; one of these is homologous with ethyl, and is represented by the formula (C_nH_{n+1}); this class has been long known and extensively investigated. The second series has only recently attracted the notice of chemists; it is homologous with allyl (C_6H_5), and is represented by the formula (C_nH_{n-1}). Allyl is the only member of this series which has been carefully examined.

These two groups of hydrocarbons are intimately related to each other, and, probably, the members of the latter series will hereafter be obtained from the former, by a general method analogous to that by which Berthelot and De Luca have succeeded in obtaining allyl from glycerin (1242).

Now, intermediate between these two groups is a third, which has already been long recognised, viz. the group of the hydrocarbons which are homologous with olefiant gas, represented by the general formula $(C_{2n}H_{2n})$; and which, it may be remarked, would be produced by the combination of the *corresponding terms* of the two groups previously alluded to, $C_nH_{n-1} + C_nH_{n+1} = C_{2n}H_{2n}$. It is only recently that these hydrocarbons have been regarded as radicles; yet they are undoubtedly compounds of this nature, but they differ essentially from the radicles of the two other groups, inasmuch as their molecules are *biatomic*, or are capable of displacing two equivalents of hydrogen; whilst the radicles typified by ethyl and allyl are uniatomic, and only represent one equivalent of hydrogen.

We have already examined the nature of Dutch liquid (400), a compound the molecular composition of which was then indicated by the formula (C_4H_3Cl,HCl): the view thus represented harmonises well with the decompositions which Dutch liquid experiences when treated with potash; but the compound may also be regarded as the result of a combination of the diatomic radicle (C_4H_4) with two equivalents of chlorine, thus $(C_4H_4)''Cl_2$, and as such it may be termed *bichloride of ethylene*; the biatomic character of ethylene $(C_4H_4)''$ being indicated here by the notation $('')$ affixed to the radicle.* Bromine and iodine also combine with olefiant gas, and form corresponding compounds $(C_4H_4)''\,Br_2$; and $(C_4H_4)''\,I_2$.

(1185) *Glycol* $\left[C_4H_6O_4 = (C_4H_4)''\,O_2, \left.\begin{matrix}H\\H\end{matrix}\right\}O_2\right]$.—When biniodide of ethylene $(C_4H_4I_2)$ is triturated with anhydrous acetate of silver, in the proportion of ten parts or one equivalent of the former to twelve parts or two equivalents of the latter, and the mixture is introduced into a flask, a brisk reaction speedily begins to take place; the temperature rises, and the mass becomes yellow, owing to the formation of iodide of silver; while carbonic acid and olefiant gas, the result of a secondary decomposition, are evolved in abundance. Wurtz recommends that the materials be mixed in quantities of 150 grains of the biniodide of ethylene, and 180 grains of the acetate of silver; and as soon as the reaction has terminated, fresh portions are to be added until 1500 or 2000 grains of the biniodide have been employed. The product of this reaction is then to be submitted to distillation, and the portions which distil over between 320° and 392° are to be collected separately, and rectified from litharge. By repeating the distillation and collecting the product in separate portions, a liquid is at length obtained which boils at 365°, and may be distilled without undergoing decomposition. This liquid is the *binacetate of glycol*, and if the secondary products of the reaction be neglected, its formation may be thus represented:—

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* Occasionally we shall find it convenient to indicate the biatomic character of a group by the marks $('')$, or teratomic character by the marks $(''')$, though in most instances these marks will be omitted.

$$\overbrace{C_4H_4I_2}^{\text{Biniodide of Ethylene.}} + \overbrace{2\,(AgO,\,C_4H_3O_3)}^{\text{Acetate of Silver.}} = 2\,AgI + \overbrace{(C_4H_4)O_2,\,2\,C_4H_3O_3}^{\text{Binacetate of Glycol.}}.$$

Binacetate of glycol is a colourless neutral liquid, which emits a faint acetic odour when heated. It is heavier than water, in which it is but slightly soluble: alcohol dissolves it freely.

Bibenzoate of glycol appears to be formed when biniodide of ethylene is acted upon by anhydrous benzoate of silver, and other salts of silver likewise attack the biniodide of ethylene with facility, so that various compound glycolic ethers may be obtained without difficulty.

When binacetate of glycol is digested upon powdered hydrate of potash, an energetic action speedily commences; but the mixture must be maintained at a temperature of about 360° for a few hours, in order that the decomposition may be complete: if it be then submitted to distillation, glycol passes over, and may be purified by fractionated distillation.

Glycol is a colourless, slightly viscous liquid, with a sweet taste. It boils at about 383°, and may be distilled unaltered: its vapour is inflammable. It is soluble in water, and in alcohol, in all proportions. It differs in composition, from ordinary alcohol by containing two equivalents more of oxygen. It is evidently a biatomic alcohol, the radicle of which is capable of supplying the place of two equivalents of hydrogen. Wurtz represents the base acetylia (C_4H_5N; 1069) as ammonia, containing one equivalent of the dibasic radicle ethylene $(C_4H_4)''$ in place of two equivalents of hydrogen, and it is obvious that acetylia may be viewed, either as $\left.\begin{matrix}C_4H_3\\H\\H\end{matrix}\right\}N$, or as $\left.\begin{matrix}(C_4H_4)''\\H\end{matrix}\right\}N$.

There can be little doubt but that glycol is the type of a new class of homologous alcohols, each of which will form the starting point of numerous series of collateral derivatives. Indications of the formation of *tritylic glycol*, and of an acetin derived from *ethylic glycerin*, have already been obtained.

The relations of the uniatomic, biatomic, and teratomic alcohols to water may be thus exemplified :—

$\overbrace{\text{Type .}\ \left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Uniatomic Alcohols.}}$	$\overbrace{\text{Type .}\ \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_4}^{\text{Biatomic Glycols.}}$	$\overbrace{\text{Type .}\ \left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_6}^{\text{Teratomic Glycerins.}}$
$\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Ethylic Alcohol.}}$	$\overbrace{\left.\begin{matrix}(C_4H_4)''\\H_2\end{matrix}\right\}O_4}^{\text{Glycol.}}$	$\overbrace{\left.\begin{matrix}(C_4H_5)'''\\H_3\end{matrix}\right\}O_6}^{\text{Ethylic Glycerin (?)}}$
$\overbrace{\left.\begin{matrix}C_6H_7\\H\end{matrix}\right\}O_2}^{\text{Tritylic Alcohol.}}$	$\overbrace{\left.\begin{matrix}(C_6H_6)''\\H_2\end{matrix}\right\}O_4}^{\text{Tritylic Glycol (?)}}$	$\overbrace{\left.\begin{matrix}(C_6H_5)'''\\H_3\end{matrix}\right\}O_6}^{\text{Ordinary Glycerin.}}$

CHAPTER VII.

ESSENTIAL OILS AND RESINS.

§ I. Essential Oils.

(1185 *bis*) The odoriferous principle of most plants resides in certain compounds consisting chiefly of carbon and hydrogen ; and although the boiling-point of these bodies lies considerably above 212°, they emit at ordinary temperatures minute quantities of an intensely odorous vapour. They have a certain resemblance to the fixed oils in their inflammability, sparing solubility in water, and ready solubility in alcohol and in ether ; as well as in the production of a greasy stain when dropped upon paper, though this mark is only transient ; and they feel harsh instead of unctuous when rubbed upon the skin : from the points of their similarity to the oils, and from the fact of their constituting in many cases the distinctive compound of the plant which yields them, they are termed *essential* or *volatile oils.*

The production of the essential oils is not limited to any particular portion of the vegetable organism. In some natural families, as for instance, in the *Umbelliferæ,* the oil is most abundantly contained in the seeds. The *Aurantiaceæ* yield two different kinds of essential oil, one of which is obtained from the flower, and the other from the rind of the fruit. The *Myrtaceæ* and the *Labiatæ* supply it from the leaves, whilst the *Rosaceæ* contain it only in the petals of the flower.

Generally speaking, the oils appear to exist ready formed in the plant, being enclosed in little sacculi, which are often visible to the naked eye, as in the leaves of the *Myrtaceæ*, and the peel of the *Aurantiaceæ*. In a few cases, such as those of the oils of bitter almonds and of mustard, they are produced by a species of fermentation operating on a principle contained in the cells of the seed; this change does not commence until the seed has been crushed and mixed with water. A peculiar azotized body present in the seed is thus brought into contact under favourable circumstances with the compound which yields the oil, and the peculiar aroma of the essence is speedily developed.

The oils of lemon and of orange are extracted by simple pressure of the rind of the fruit; but the general process of extraction consists in placing the appropriate portions of the plant in a still, with water, and applying heat; in order to prevent the vegetable materials from being over-heated by resting against the sides of the still, which would give to the distillate a disagreeable odour, it is customary to suspend them in a net or perforated metallic vessel in the upper part of the still. A better method of obtaining the essence is to allow steam to pass over the plant, and to condense the vapour afterwards in the usual way. The presence of steam favours the volatilization of the oils at a comparatively low temperature, for it mechanically carries over the vapour: the distillate is at first milky, but the greater portion of the essence separates from the milky liquid on standing. The water which is condensed in the receiver with the oil acquires the odour and taste of the essence; such waters constitute the fragrant *distilled waters* of the apothecary: by a second distillation, these waters are freed from some impurities which are mechanically carried over, and which would cause the liquid to become mouldy and would destroy its fragrance. A small portion only of the essential oil is retained in solution in the distilled water, and the greater portion of the oil which is thus retained may be separated by saturating the liquid with chloride of sodium; the essence on standing rises to the surface. It may also be removed by agitating the distilled water with ether, which dissolves the oil; and on expelling the ether from the layer which separates on standing, the pure oil is procured. In some cases where the essence becomes altered during the act of distillation, the fragrance of the plant is obtained and concentrated by dissolving it in a fixed oil, which is itself destitute of odour, such as oil of poppy seeds. The leaves of the flower are in such instances spread in thin layers upon woollen cloths saturated with the fixed oil, the cloths thus charged are then piled one upon another, and submitted to the action of a press.

The essential oils vary in specific gravity, but in general they are lighter than water. The oils are usually liquid at ordinary temperatures, but oil of aniseed is solid at all temperatures below 60°. If cooled slowly, many of them separate into a solid and a fluid portion, respectively termed *stearopten* and *elæopten*. This fact is readily explained by the circumstance that most of the essential oils are mixtures of two or more distinct chemical compounds which differ in volatility and fusibility; one of these compounds generally contains no oxygen, whilst the others are often substances formed from it by oxidation. Of these the pure hydrocarbon is generally the more volatile; it acts as a solvent to the oxidized compounds, which, by a depression of temperature, may frequently be separated from it in a crystallized form.

Most of the essential oils have a yellowish colour, which deepens when exposed to the air; during such exposure they absorb oxygen more or less rapidly, and are thus gradually converted into a solid, resinous, or camphreous mass. Those oils which absorb oxygen the most rapidly have in general the most powerful odour. This absorption of oxygen is sometimes attended with a simultaneous extrication of carbonic acid and water: this occurs in the case of the oils of anise, and of lavender; and in such instances the resulting resinous mass is not a simple oxide of the hydrocarbon.

The essential oils are insoluble in potash, and are not capable of saponification by treatment with alkalies: but if the oils be transmitted in the form of vapour over heated hydrate of potash, hydrogen is frequently disengaged, and the oil becomes oxidized, forming an organic acid which enters into combination with the potash. Oil of cinnamon may thus be converted into cinnamate of potash:—

$$\overbrace{C_{18}H_8O_2}^{\text{Oil of Cinnamon.}} + KO, HO = \overbrace{KO, C_{18}H_7O_3}^{\text{Cinnamate of Potash.}} + 2\,H.$$

Chlorine, iodine, and bromine act upon most of the essential oils, and form compounds in which a certain number of equivalents of these elements displace a corresponding number of equivalents of hydrogen. Nitric acid oxidizes most of the essential oils with great violence.

The essences may be arranged under three principal divisions, viz.:—*A*. Pure hydrocarbons; *B*. Oxidized essences; *C*. Sulphuretted essences.

The pure hydrocarbons are generally lighter than water; the other two varieties often have a specific gravity greater than that of water.

The essences which belong to the first class always occur in a state of admixture with a larger or smaller proportion of an oxidized compound.

(*A.*) *Pure Hydrocarbons.*

(1186) The group of chemical compounds formed by the essential oils which contain no oxygen presents many interesting features: sixteen or twenty of these substances are isomeric. These isomeric bodies may be subdivided into two metameric classes; in one of which the molecule is represented by $C_{20}H_{16}$; to which class oil of turpentine belongs; in the other, the molecule of the oil, like that of essence of cubebs, is represented by $C_{30}H_{24}$. The members of each of these groups, notwithstanding the diversity of their odour and taste, are strictly metameric; equal weights yielding exactly equal volumes of vapour. The first of these groups, the members of which are termed *terebenes* or *camphogens*, is the more numerous and important. Many characters, both chemical and physical, are common to all the members of the group: for example, they have a specific gravity in the liquid form closely approaching to 0·860; and the boiling-point, though subject to greater variations, in most instances is very near 320°.

Many of the terebenes cannot be distinguished from each other except by their action upon polarized light; some varieties of oil of turpentine, for example, cause left-handed rotation of a ray of polarized light; oil of lemons produces rotation to the right hand; whilst other oils are destitute of rotatory action upon the plane of polarization. A slight change in the molecular arrangement of the constituent particles of these bodies modifies their action upon polarized light, for it has been found that oil of turpentine by peculiar treatment at a high temperature may be deprived of its rotatory power, although it retains its usual chemical properties (1189).

The terebenes rapidly absorb dry hydrochloric acid gas, and yield compounds termed *artificial camphors;* some of these bodies crystallize, and in appearance and properties much resemble natural camphor; while others of the oils form combinations with the acid equally definite, but which retain the liquid form. Oil of turpentine and oil of lemons both form solid compounds with hydrochloric acid as well as liquid ones; but the oils of black pepper and of bergamotte form only liquid compounds :—

Artificial Camphors.		
From oil of turpentine	solid	$C_{20}H_{16}$, HCl
From oil of lemons . .		$C_{20}H_{16}$, 2 HCl
rom oil of black pepper	liquid	$5(C_{20}H_{16})$ 8 HCl
om oil of bergan		$3(C_{20}H_{16})$ HCl, HO.

Analogous compounds with the other hydracids, such as the hydrobromic, and the hydriodic, may also be obtained.

Another remarkable feature of the terebenes is the power which they possess of combining with water, and thus forming solid volatile crystalline substances which have a still closer analogy to camphor both in composition and properties than the hydrochloric compounds. Mere contact of the oil with water, or with alcohol slightly acidulated with nitric acid, in most instances gives rise to these compounds; oil of turpentine furnishing not fewer than three such hydrates, viz.; *terpine* ($C_{20}H_{16}$, 4 HO, 2 Aq); ($C_{20}H_{16}$, 4 HO); and *terpinol*, ($C_{20}H_{16}$, HO); the first two are solid, the last is liquid. Oil of lemons gives two such compounds, viz.; ($C_{20}H_{16}$, 6 HO) and ($C_{20}H_{16}$, 4 HO); and oil of juniper one such hydrate ($C_{20}H_{16}$, 4 HO): the camphor of the *Dryobalanops camphora*, or Borneo camphor, consists of $C_{20}H_{16}$, 2 HO.

All these varieties of camphor when distilled with anhydrous phosphoric acid, lose their water, and yield hydrocarbons, having the composition $C_{20}H_{16}$; ordinary camphor, $C_{20}H_{16}O_2$, when similarly treated, also gives a hydrocarbon termed cymole ($C_{20}H_{14}$). Indeed, the simple act of sublimation deprives the camphor or solid hydrate ($C_{20}H_{16}$, 6 HO) of the oils of turpentine, of lemon, and of bergamotte of two equivalents of their water; the sublimed camphor in each case being represented by the formula, $C_{20}H_{16}$, 4 HO.

The terebenes when exposed to the air absorb oxygen; they become brown and viscid; and are ultimately converted into resins. In many instances this oxidation may be regarded as a simple substitution of oxygen for hydrogen, the number of equivalents of oxygen absorbed corresponding exactly to the number of equivalents of hydrogen removed in the form of water, but in other cases this constitutes only the first stage of the process, and an additional quantity of oxygen combines with the newly formed oxide; a good example of the latter mode of oxidation is seen in the conversion of the liquid oil of lemons into the solid:—

$$C_{20}H_{10}H_6 + O_{16} = C_{20}H_{10}O_6, O_4, + 6\ HO.$$

(1187) OIL OF TURPENTINE ($C_{20}H_{16}$). *Sp. gr. of liquid* 0·864; *of vapour* 4·76.—Various species of pine, when wounded, pour out a semisolid resin, of which there are different varieties: that obtained from the *Pinus abies* constitutes *common turpentine*; that from the larch is known as *Venice turpentine*; and that from the *Pistacia lentiscus* forms *Chian turpentine*.

If the turpentine of the *Pinus abies*, or of the *Pinus sylvestris*, be distilled with water, it yields nearly one-fourth of its weight of essential oil: this oil passes over with the vapour of water as a volatile, limpid, very inflammable liquid, of a penetrating well-known balsamic odour. The residue in the retort constitutes common *rosin* or *colophony*. Oil of turpentine boils at 320°, and may be distilled unchanged. It mixes freely with alcohol and ether, but not with water; it dissolves the fixed and essential oils, and is largely used in the preparation of many kinds of varnish, since it readily dissolves the resins, and on volatilizing leaves them behind in the form of a transparent coating upon the surface of the objects to which it had been applied. Oil of turpentine dissolves sulphur and phosphorus with facility; it is also one of the best solvents for caoutchouc. Most of the *camphine* sold in England produces a right-handed rotation, and is said to be furnished by the *Pinus australis* of the southern States of North America.

Commercial oil of turpentine frequently consists of a mixture of several isomeric hydrocarbons, which act differently on polarized light. The rotation occasioned by Bordeaux turpentine, which is produced chiefly from the *Pinus maritima*, is left-handed, but the amount of the rotation varies in different samples, according to the proportion in which the oils are mingled. According to Berthelot, if the ordinary Bordeaux turpentine be distilled *in vacuo*, after saturating the acids which it contains, a homogeneous hydrocarbon, *terebenthene*, (*sp. gr.* 0·864, *at* 59°) is obtained. It boils between 318° and 325°. It is endowed with left-handed rotatory action upon a polarized ray to a definite extent.

(1188) *Modifications of Oil of Turpentine.*—Deville (*Ann. de Chimie*, II. lxxv. 37, and III. xxvii. 80) and Berthelot (*Ib.*, III. xxxix. 5) have carefully studied the modifications of which oil of turpentine is susceptible without undergoing any change in the proportion of its components. Some of these modifications retain their rotatory power upon polarized light, whilst others are inactive in this respect:—

a. Active Modifications.—When English essence of turpentine is simply heated in a closed vessel to 460° or 480°, it becomes converted into a mixture of several compounds, which boil at different temperatures; two of these, *isoterebenthene* and *metaterebenthene*, may be separated from each other by fractionated distillation. These modifications may be produced at a lower temperature if the essence be heated with water, or with the chloride of calcium, of strontium, of zinc, or of ammonium. Fluoride of calcium, as well as many organic acids, such as the acetic, oxalic and tartaric, also produces similar effects.

1. *Isoterebenthene* (*Sp. gr.* 0·843, *at* 71°).—This is a colourless liquid having an odour of stale lemons. It boils at about 350°.

It exerts a left-handed rotation upon polarized light, but the intensity of this power appears to vary with the duration and intensity of the heat to which it has been exposed. It may be made to yield a crystalline hydrate, and a solid hydrochlorate.

2. *Metaterebenthene* (*Sp. gr.* 0·913, *at* 68°).—This body forms at least one-third of the entire quantity of the essence submitted to heat; it constitutes the residue left in the retort after all the matters volatile below 660° have been expelled. It may be volatilized without decomposition at a temperature somewhat beyond this. It is a viscous yellowish body, possessed of a strong disagreeable odour, and a tendency to rapid oxidation. It exerts a left-handed rotatory power upon polarized light.

Intermediate between these two bodies are other isomeric compounds, of intermediate boiling-points; but they have not been specially examined.

b. Inactive Modifications.—Besides these modifications which retain their rotatory power, four other forms of the essence have been procured, which exert no action upon polarized light. These substances are:—

1. Terebene
2. Colophene
3. Camphilene or dadyl
4. Terebilene or peucyl.

The first two have been obtained by acting upon oil of turpentine with sulphuric acid; the last two by decomposing artificial camphor by means of quicklime (1189).

In order to procure terebene and colophene, Deville mixes oil of turpentine with about $\frac{1}{20}$th of its weight of oil of vitriol, in a flask which is artificially cooled. After brisk agitation, the mixture becomes viscous and of a dark red colour. It must be left at rest for twenty-four hours, during which time it separates into two layers, the lower one being nearly black and strongly acid. The clear liquid is then to be decanted and gently heated: bubbles of sulphurous acid escape, and the colour gradually disappears, whilst the liquid becomes converted into a mixture of terebene and colophene. Upon subjecting the mixture to distillation, terebene passes over in the first portions, and when rectified from a fresh portion of oil of vitriol, is obtained in a state of purity. The last portions of the distillate consist of colophene.

Terebene has a characteristic odour, resembling that of oil of thyme. It boils at the same temperature as the unmodified essence of turpentine, yielding a vapour of the same density, but it is less prone to oxidation. It combines with hydrochloric acid, and forms a liquid compound, $2\,(C_{20}H_{16})\,HCl$.

Colophene (*Sp. gr. of liquid* 0·940) yields a vapour, the density of which is twice as great as that of terebene, with which it is polymeric. It absorbs hydrochloric acid, and forms with it a compound of the colour of indigo. In order to obtain colophene in a state of purity, it must be rectified from an alloy of potassium and antimony (703). Colophene may also be produced by the distillation of colophony, from which it derives its name. When viewed by direct light it is colourless, but it exhibits the fluorescent character in so marked a degree, that in particular directions it appears of a deep indigo blue. It is slightly viscous, and boils between 590° and 600°.

(1189) *Artificial Camphors, and Oils obtained from them.*—It has already been stated that essence of turpentine combines with hydrochloric acid, with which it may be made to form two compounds, $C_{20}H_{16}$, 2 HCl; and $C_{20}H_{16}$, HCl.

The first of these bodies may be obtained by allowing the essence of turpentine to remain for some weeks in contact with an excess of a solution of concentrated hydrochloric acid. It forms flattened rectangular prisms, which have an aromatic odour resembling that of oil of thyme. It is fusible at 111°, and is decomposed by distillation.

The second compound ($C_{20}H_{16}$, HCl) is obtained by transmitting dry hydrochloric acid gas into the artificially cooled essence of turpentine so long as it is absorbed. As soon as this absorption ceases, the compound must be submitted to the action of a freezing mixture of snow and salt, by which it is separated into two portions, one of which crystallizes, whilst the other remains liquid, even at 0° F. The production of the liquid compound is favoured by elevation of temperature; if the temperature of the essence be raised to 212° during the absorption of the hydrochloric acid, the liquid compound only is formed. Both the solid and the liquid portion are found, on analysis, to possess the same composition ($C_{20}H_{16}$, HCl). The solid body has been termed *hydrochlorate of camphene* or *of dadyl.* It crystallizes in white prisms, which have an aromatic smell and taste, resembling that of ordinary camphor. It is insoluble in water; alcohol dissolves one-third of its weight of it. This artificial camphor melts at 239°, and boils at 329°, at the same time undergoing partial decomposition.

Camphene, Camphilene or *Dadyl.*—If the vapour of this hydrochloric compound be transmitted over heated quicklime, it is decomposed, chloride of calcium and water are formed, and a body termed *camphilene* (Deville), having the composition of oil of turpentine, is liberated; this body may again be combined with hydrochloric acid, in which case the solid artificial camphor is reproduced. Camphilene boils at 273°. It is entirely devoid of the power of rotation upon a ray of polarized light.

The liquid hydrochlorate has been termed ***hydrochlorate of peucyl:*** it is somewhat viscous, and has a sp. gr. of 1·017. If it be distilled with quicklime, ***terebilene*** (Deville), another hydrocarbon isomeric with essence of turpentine, comes over; it possesses no rotatory power upon polarized light. When again combined with hydrochloric acid, it furnishes a liquid uncrystallizable compound.

Oil of turpentine is not the only one of these essential oils or hydrocarbons which exhibits this remarkable facility of assuming different isomeric states under the influence of heat and of acids. Oil of lemons produces an analogous, though different series of modified products, and most probably the greater number of the essential oils, which are isomeric with oil of turpentine, would be found to furnish like results when subjected to similar treatment.

Hydrates of Oil of Turpentine.—Mention has been already made (1186) of the power which oil of turpentine possesses of slowly combining with water, and forming crystalline compounds. One of these, ($C_{20}H_{16}$, 6 HO) may be obtained in the form of rhomboidal prisms, by agitating together frequently, for two or three days, a mixture of 4 measures of oil of turpentine, 1 of nitric acid, sp. gr. 1·36, and 3 of alcohol, sp. gr. 0·840. In the course of a month or six weeks, especially if it be exposed to the sun's rays, voluminous crystals are formed. This hydrate is soluble in 22 parts of boiling water, from which it crystallizes on cooling. It is also freely soluble in alcohol, ether, oil of turpentine, and acetic acid. When sublimed it loses 2 equivalents of water, and is converted into the hydrate with 4 HO.

The hydrate ($C_{20}H_{16}$, 4 HO) may also be procured when oil of turpentine and water are brought into contact, especially if the temperature be maintained at about 120°: the crystals of this substance fuse at 302°, and boil at 482°. It may be sublimed without being decomposed, and yields a vapour of the sp. gr. 6·257. When exposed to the air it absorbs water, and becomes reconverted into the hydrate with 6 HO.

A third hydrate, termed *terpinol* ($C_{20}H_{16}$, HO, *Sp. gr.* 0·852), which is liquid at ordinary temperatures, may be obtained by dissolving either of the preceding hydrates in boiling water, adding a little hydrochloric or sulphuric acid, and distilling. Terpinol passes over as an oily liquid, with an odour like that of hyacinths. It boils at 334°.

(1189 *bis*) *Products of the Oxidation of Oil of Turpentine.*—Besides the resins which are formed by the spontaneous oxidation of essence of turpentine, various compounds may be obtained from it by artificial processes of oxidation.

When the essence is distilled with bichromate of potash and sulphuric acid, formic acid is produced abundantly. If it be distilled with water and chloride of lime, a copious extrication of carbonic acid takes place with tumultuous violence, and chloroform is found in the products of the distillation. Chlorine acts violently upon oil of turpentine, the reaction being often attended with sufficient heat to inflame the mixture.

If oil of turpentine be heated gently with oxide of lead, it absorbs oxygen rapidly, and becomes converted into formic and *teretinic* acids, which enter into combination with the oxide of lead:—

$$\overbrace{C_{20}H_{16}}^{\text{Oil of Turp.}} + O_{14} = \overbrace{C_{18}H_{14}O_{10}}^{\text{Teretinic Acid.}} + \overbrace{HO,\ C_2HO_3}^{\text{Formic Acid.}}.$$

Teretinic acid is soluble in alcohol, from which it may be obtained crystallized in tufts of delicate colourless needles: it is insoluble in water. Most of the compounds of this acid with the metallic oxides are insoluble in water, but soluble in alcohol.

If a few teaspoonsful of essence of turpentine be introduced into a jar nearly filled with oxygen gas, standing over water, and exposed to the rays of the sun, the interior of the jar speedily becomes coated with brilliant crystals of *hydrated oxide of turpentine* ($C_{20}H_{16}O_2$, 2 HO). This substance may be dissolved in alcohol, from which it may be obtained in crystals. It is also soluble in ether and in boiling water.

Nitric acid acts violently upon oil of turpentine; the two liquids must, therefore, be mixed very cautiously. As the result of the action, a yellow resin is formed, and a quantity of oxalic and terebic acid (1253), besides three other acids, one of which is fusible and may be sublimed; it is termed *terebenzic acid* (HO, $C_{14}H_6O_3$). The second is isomeric with phthalic acid, and is hence termed *terephthalic acid* (HO, $C_8H_2O_3$); it is insoluble in water, alcohol, and ether. The third is termed *terechrysic acid* (HO, $C_6H_3O_4$) in allusion to its yellow colour; it is very soluble in water, and is not susceptible of crystallization.

(1190) *Other Essences which yield oils isomeric with Oil of Turpentine.*—The following are some of the principal essences which are metameric or isomeric with oil of turpentine:—

1. *Oil of Bergamotte* (*Sp.gr.* 0.869), which is obtained from the rind of the ripe fruit of the bergamotte or lime, consists of two portions, viz., a hydrocarbon ($C_{20}H_{16}$), and a solid substance ($C_{30}H_{10}O_{10}$), which may be supposed to be formed from the liquid essence by oxidation, $3\ (C_{20}H_{16}) + O_{48} = 2\ (C_{30}H_{10}O_{10}) + 28\ HO$.

2. *Oil of Lemons* also contains a solid oxidized essence in small quantity ($C_{20}H_{10}O_{10}$), but the bulk of the oil consists of a hydrocarbon ($C_{20}H_{16}$), which may be obtained in a state of purity by distilling the crude essence. This hydrocarbon is susceptible of a variety of modifications, analogous to those which may be produced in oil of turpentine. The essential oil from the rind of the *orange* appears to be identical with the essence of lemons.

3. *Oil of Neroli* is the fragrant oil obtained from the blossoms of the orange tree. It is colourless when recently distilled, but becomes red by exposure to light, or by admixture with sulphuric acid. This oil also consists of a hydrocarbon $C_{20}H_{16}$, and of an oxidized portion which is solid and destitute of odour, the fragrance of the oil being due to the hydrocarbon.

4. The oil of the *common birch*, which is used in the preparation of Russia leather, to which it imparts its agreeable odour, is obtained from the tar furnished by the imperfect combustion of the bark of the tree. It consists of a mixture of several oils, amongst which the principal is the hydrocarbon $C_{20}H_{16}$, which may be isolated by repeated fractionated distillation.

5. *Essence of Camomile*: of this there are two varieties, one of which is obtained from the *Anthemis nobilis*; it is of a greenish colour, and consists of a hydrocarbon ($C_{20}H_{16}$), and an oxidized portion ($C_{10}H_8O_2$?), which when heated with hydrate of potash is converted into angelate of potash ($KO, C_{10}H_7O_3$), with evolution of hydrogen (1175). The second variety is obtained from the *Matricaria chamomilla*. It is remarkable for its deep blue colour: it contains an oxidized oil ($C_{20}H_{16}O_2$), which has the composition of laurel camphor. It may be distilled without change, and remains liquid below 32°.

The oil of the *Achillea millefolium* is also distinguished by its beautiful blue colour, but it has not been minutely examined.

6. *Essence of Juniper* boils at 320°. It produces left-handed rotation on a ray of polarized light, and if left in contact with water gradually deposits a white crystalline hydrate ($C_{20}H_{16}, 2\,HO$).

(1191) 7. *Oil of Carraway* (*Sp. gr.* 0·938) is obtained from the seeds of the *Carum carvi*; it consists of two portions; the hydrocarbon ($C_{20}H_{16}$) has been termed *carvene*; the oxidized portion is known as *carvole*. Carvene is a very fluid, colourless oil, lighter than water, with a slight agreeable odour and an aromatic taste; it absorbs hydrochloric acid gas, and forms with it a crystallizable solid which melts at 123°. Carvole, $C_{20}H_{14}O_2$, is a liquid of sp. gr. 0.953°; it boils at about 437° (Voelckel). It yields a liquid camphor ($C_{20}H_{14}O_2$ HCl) with hydrochloric acid. With sulphuretted hydrogen carvole yields a compound termed *hydrosulphate of carvole* ($C_{20}H_{14}O_2$, HS): this substance is obtained by agitating the less volatile portion of oil of carraway with an equal bulk of alcohol recently saturated with ammonia and sulphuretted hydrogen; it is deposited in yellowish crystals, which may be recrystallized from boiling alcohol; they may be volatilized without decomposition. If this compound be agitated with an alcoholic solution of potash it is decomposed, pure carvole is liberated and dissolved by the alcohol, and on the addition of water it rises to the surface in the form of an oily layer.

(1192) 8. *Oil of Cloves* (*Sp. gr.* 1·055 – 1·060).—The berries of the pimento and the unexpanded buds of the *Caryophyllus aromaticus* or "cloves," yield an essential oil which is not solidified by a cold of 0° F. It consists chiefly of a hydrocarbon isomeric with oil of turpentine, holding in solution an acid body termed *eugenic acid* ($C_{20}H_{12}O_4$?). This acid forms a colourless liquid of sp. gr. 1·079, which emits the odour of oil of cloves. It boils at 469° (Ettling), and forms crystallizable salts with the alkalies. Two other crystallizable substances are obtained from oil of cloves; one of them is named *eugenin*, and is said to be isomeric with eugenic acid. The other, termed *caryophyllin*, $C_{20}H_{16}O_2$, is isomeric with ordinary camphor; it is gradually deposited from the oil in crystalline needles.

9. *Oil of Ginger* (*Sp. gr.* 0·893) is yellow, and intensely burning and aromatic. It boils at about 475°. It appears to have the composition of a hydrate of a hydrocarbon isomeric with oil of turpentine, 4 ($C_{20}H_{16}$) 5 HO.

(1193) 10. *Oil of Cubebs* (*Sp. gr.* 0·929).—When cubebs (*Piper cubeba*) are distilled with water, they furnish an essence which is colourless and somewhat viscous; it has a camphreous, aromatic taste. It boils a little below 500°, and when distilled yields a hydrocarbon which furnishes a crystalline compound with hydrochloric acid, consisting of ($C_{30}H_{24}$, 2 HCl). This substance fuses at 268°. When essence of cubebs is re-distilled with water, it deposits a species of camphor ($C_{30}H_{24}$, 2 HO), which melts at 154°, and may be distilled at 302° without decomposition. The essence of cubebs, therefore, though isomeric with oil of turpentine, appears to contain the hydrocarbon in a more condensed form, viz., as ($C_{30}H_{24}$).

11. *Essence of Cajeput*, (*sp. gr.* 0·978,) which is obtained by distilling balsam of cajeput with water, appears to belong to the same class as that of cubebs. It boils at 500°, undergoing partial decomposition. It yields a crystalline compound with hydrochloric acid ($C_{30}H_{24}$, 3 HCl).

(1194) 12. *Essence of Hops.*—This essence is obtained by distilling dried hop cones with water. The oil when first obtained is of a beautiful green colour, but it is rendered colourless by rectification. It remains liquid at 1° F., and begins to boil at about 284°, but the boiling-point rises rapidly till it exceeds 600°. Its odour somewhat resembles that of the hop. When exposed to the air it becomes converted into an acid resinous mass. Oil of hops is a mixture of the hydrocarbon $C_{20}H_{16}$, with *valerole* ($C_{12}H_{10}O_2$). The hydrocarbon may be obtained in a pure form by allowing the oil to fall drop by drop upon hydrate of potash, when carbonate and valerate of potash are formed:—

$$\overbrace{C_{12}H_{10}O_2}^{\text{Valerole.}} + 3(KO, HO) + 2\,HO = 2(KO, CO_2) + \overbrace{KO, C_{10}H_9O_3}^{\text{Valerate of Potash.}} + 6\,H.$$

13. *Essence of Valerian* also consists of valerole and of a hydrocarbon $C_{20}H_{16}$, which is identical with borneëne, the hydrocarbon which accompanies Borneo camphor (1200). By distilling off the essence at a temperature of 392°, the borneëne may be expelled. Valerole when exposed to a temperature of 32° crystallizes in transparent prisms, which do not melt until heated to 68°. It gradually becomes oxidized by exposure to the air, and the disagreeable odour of valeric acid is developed. In its pure form its odour is but slight, resembling that of hay. Sulphuric acid dissolves it, and forms a blood-red solution, which contains a colligated sulpho-acid.

(1195) 14. *Oil of Thyme.*—This consists of an oxidized portion, *thymole*, and of a hydrocarbon, *thymene*. The latter constitutes the more volatile portion of the oil; it has an agreeable odour of the plant: it boils at 329°, and exerts no action on polarized light. *Thymole*, $C_{20}H_{14}O_2$, is isomeric with cuminic alcohol; it has the agreeable odour of thyme, and constitutes about one-half of the essence of thyme. It is a solid which crystallizes in oblique rhombic prisms: it fuses at 111° and boils at 446°, giving off a vapour of sp. gr. 5·51. It is very soluble in alcohol and in ether. This substance is also contained in the oil of horse-mint (*Monarda punctata*), and in an Indian plant, the *Ptychotis ajowan*. Thymole combines with sulphuric acid and forms a colligated acid, the *sulphothymylic* ($HO, C_{20}H_{13}O, S_2O_6$), which is analogous to the sulphethylic.

According to Lallemand, when thymole is treated with oxidizing agents such as chromic acid, or a mixture of peroxide of manganese and sulphuric acid, it yields a substance termed *thymoile* ($C_{24}H_{16}O_4$),* which sublimes in brilliant orange-coloured quadrangular plates, of an aromatic odour and an appearance resembling that of kinone (1127), with which it is homologous. If treated with sulphurous acid or other reducing agents, it combines with hydrogen and yields *thymoilole* ($C_{24}H_{18}O_4$), the homologue of hydrokinone; and by mixing a solution of equal weights of thymoile and thymoilole in boiling alcohol, the liquid immediately becomes of a deep red colour, and deposits beautiful violet-coloured prismatic crystals, which have a bronze lustre. These correspond to what has been termed green hydrokinone.

(1196) *Essences which contain other Hydrocarbons.*—1. *Oil of Peppermint.*—This essence when distilled with anhydrous phosphoric acid, yields a hydrocarbon termed *menthene*, $C_{20}H_{18}$. The essence also appears to contain a solid hydrate of this compound ($C_{20}H_{18}$, 2 HO), which is analogous to camphor: this substance may be obtained in crystals; it fuses at 93° and boils at 416°, emitting a vapour of sp. gr. 5·62.

2. Essence of *Cedar wood* is somewhat analogous in its nature to the foregoing oil. It consists of a crystallizable solid ($C_{32}H_{28}O_2$) dissolved in a hydrocarbon ($C_{32}H_{26}$), which has been termed *cedrene*.

3. *Attar of Roses* consists also of two compounds, one of which has but little odour; it remains solid at temperatures below 203°, and boils at about 592°. It is polymeric with olefiant gas. The fragrant portion is liquid; it contains oxygen, but its composition is not accurately known.

The following table includes a list of the more important essences which contain unoxidized hydrocarbons:—

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* It is probable that the formula both of kinone and of thymoile should be represented as one-half of that given by Gerhardt and Lallemand; so that thymoile should be represented as $C_{12}H_8O_2$, since it is not easy to see how a body which, like thymol, contains in its molecule only 20 equivalents of carbon, should by oxidation yield a compound containing 24 equivalents of carbon.

Table of Essential Oils not containing Oxygen.

	Oils.	Formula.	Sp. gr.		Boiling point °F.	Direction of rotation.	Compound with HCl.	Remarks.
			Liquid.	Vapour.				
From Oil of Turpentine.	Terebenthene	$C_{20}H_{16}$	0·864	4·812	318—325°			Many of the oils enumerated in this table contain oxidized compounds in addition to the hydrocarbon,—as may be seen below.
	Isoterebenthene	,,	0·843		350	left.	solid.	
	Metaterebenthene	,,	0·913		above 680°			
	Terebene .	,,	0·86		320	none.	liquid.	
	Terebilene	,,	0.843	4·767	273	none.	liquid.	
	Camphilene .	,,	0.87		273	none.	solid.	
	Bergamotte	,,	0.869		361	right.		$C_{20}H_{16}$ & $C_{20}H_{10}O_{10}$
	Borneène	,,		4·60	320	left.	solid.	
	Birch, (tar from bark) .	,,	0·847	5·28	313			Consists of several oils.
	Camomile	,,			347			$C_{20}H_{16}$ & $C_{10}H_8O_2$
	Carraway	,,	0·938	5·17	343	right.	solid.	$C_{20}H_{16}$ & $C_{20}H_{14}O_2$
	Cloves .	,,	0·918		289		liquid.	$C_{20}H_{16}$ & $C_{20}H_{12}O_4$
	Elemi . .	,,	0·849		345	left.	solid & liquid.	
	Hop . .	,,				right.		$C_{20}H_{16}$ & $C_{12}H_{10}O_2$
	Juniper .	,,	0·86		320	left.	liquid.	
	Lemons .	,,	0·851	4·87	343	right.	solid & liquid.	Contain also $C_{20}H_{10}O_{10}$
	Orange .	,,	0·83	4·64	356	right.		
	Parsley .	,,			320			Contains an oxide.
	Pepper .	,,	0·864	4·73	333		liquid.	
	Savine. .	,,			320			
	Tolu . .	,,	0·837		320			
	Thyme .	,,		4·76	329	none.	liquid.	$C_{20}H_{16}$ & $C_{20}H_{14}O_2$
	Valerian	This hydrocarbon is Borneène					. . .	$C_{20}H_{16}$ & $C_{12}H_{10}O_2$
	Capivi. .	$C_{30}H_{24}$	0·878		500	left.	solid.	
	Cubebs .	,,	0·929		490	left.	solid.	$C_{30}H_{24}$ & $C_{20}H_{24}$, 2 HO
	Cedrene .	$C_{32}H_{26}$	0·984	7·9	458	right.		$C_{32}H_{26}$ & $C_{32}H_{28}O_2$
	Menthene	$C_{20}H_{18}$	0·851	4·94	325			From oil of peppermint.
	Colophene	$C_{40}H_{32}$	0·940		595	none.		
	Attar of Roses.	C H			592			

(*B.*) *Oxidized Essences.*

(1197) Several varieties of oxidized essential oils are known; viz.:—(*a*) Solid crystallized essences which have the composition of hydrates of a hydrocarbon; these constitute the *camphors,* of which laurel camphor ($C_{20}H_{14}$, 2 HO) is the best illustration. (*b*) *Indifferent* oils, such as spearmint oil ($C_{20}H_{20}O_2$). (*c*) Oils which resemble the *aldehyds,* such as oils of bitter almonds ($C_{14}H_5O_2$, H), and of cinnamon ($C_{18}H_7O_2$, H). (*d*) *Compound ethers,* such as oil of wintergreen (salicylate of methyl, C_2H_3O, $C_{14}H_5O_5$).

(1198) CAMPHOR.—From the statements already given it is clear that the camphors are closely related to the different varieties of turpentine. Two species of camphor are known in the east, *Borneo camphor* and *laurel camphor*; the one called Borneo camphor ($C_{20}H_{18}O_2$) is obtained from the *Dryobalanops camphora*, and is so highly prized by the natives of the east that but little of it finds its way into the European market.

Laurel Camphor ($C_{20}H_{16}O_2$) *sp. gr. of solid* 0·996; *of vapour* 5·3147.—This constitutes the common camphor of the shops. The commercial supply is furnished by the *Laurus camphora*, but it is also produced in small quantity by many other plants, which appear to furnish it by the oxidation of their essential oils. This is easily understood, since the formula of this substance is the same as that of oil of turpentine, to which two equivalents of oxygen have been added. The oils of lavender, of rosemary, and of marjoram, and those of several of the *labiatæ*, such as the oils of pennyroyal and of spearmint, contain camphor in solution. Amber, and the oils of valerian, tansy, and sage also yield it when treated with nitric acid.

Three isomeric modifications of camphor are known; they cannot be distinguished from each other, except by their action upon a ray of polarized light: one of the varieties produces rotation of the ray to the right; the second variety produces left-handed rotation; whilst the third variety has no sensible effect upon a polarized ray. The common camphor of the shops, and that obtained by the action of nitric acid upon borneène is the right-handed modification. The camphor contained in the oil of *Matricaria parthenium* exerts a left-handed rotatory action upon a ray of polarized light (Chautard); whilst, according to Biot, the camphor deposited by oil of lavender is destitute of any such rotatory effect upon a polarized ray.

In the ordinary process of extracting camphor, the wood and branches of the camphor laurel are chopped up, and placed with water in a rude kind of still, the head of which is filled with rice straw. On the application of heat the camphor rises in vapour with the water, and is condensed in the straw. It is then submitted to a second sublimation, by which means it is obtained in the form of the crude, granular camphor of commerce. This article is subsequently refined in this country by placing charges of 10 lb. or 12 lb. of the crude camphor, in large globular glass flasks, furnished with a short wide neck: heat is applied to the bottom of these flasks by means of a sand bath, and, as soon as the camphor is melted, a portion of lime is added to each flask, after which the heat is steadily maintained for forty-eight hours: during this period the camphor is slowly sublimed into the upper part of the flasks; when the operation is finished, the flasks are cooled, and at the same time broken, by sprinkling them with cold water: the pure camphor can then be removed with facility. The produce of this operation assumes the form of white, tough, translucent masses. Camphor has a peculiar odour and an aromatic taste, at first hot and afterwards cooling. It floats in water, and is sparingly soluble in this liquid; but is dissolved freely by alcohol, ether, acetic acid, and the essential oils. Although pure camphor is tough and difficult to pulverize, yet if moistened with a few drops of alcohol it may be reduced to powder with facility. When particles of powdered camphor are thrown on water, each fragment begins to be dissolved with a remarkable and rapid gyratory motion, which is instantly checked by allowing a drop of any essential oil to fall upon the surface of the water. Camphor fuses at 347°, and boils at 399°. It is very inflammable, and burns with a white smoky flame. It becomes slowly volatilized at common temperatures, and if kept in glass bottles is gradually sublimed, and condensed in octohedral crystals on the side of the vessel which is exposed to the light. If a coil of red-hot platinum wire be suspended just over a lump of camphor, the metal continues to glow, and produces a slow combustion of the camphor, which may be maintained so long as any portion remains unconsumed.

If camphor be heated under pressure with hydrate of potash, it combines with both the potash and the water; a salt termed *campholate of potash* being formed:—

$$\overbrace{C_{20}H_{16}O_2}^{\text{Camphor.}} + KO, HO = \overbrace{KO, C_{20}H_{17}O_3}^{\text{Campholate of Potash.}}.$$

When camphor is distilled with anhydrous phosphoric acid, or with dry chloride of zinc, it undergoes decomposition, and is deprived of the elements of water, whilst *cymole* is formed:—

$$\overbrace{C_{20}H_{16}O_2}^{\text{Camphor.}} = 2\,HO + \overbrace{C_{20}H_{14}}^{\text{Cymole.}}.$$

(1199) *Camphoric Acid* ($2HO, C_{20}H_{14}O_6$).—Camphor, when heated with ten times its weight of concentrated nitric acid, is slowly oxidized, and becomes converted into *camphoric acid*. This substance is sparingly soluble in water, but is freely dissolved by alcohol, as well as by ether and the essential oils. It is deposited from its solutions in the form of prismatic needles, which have a very sour taste: they are destitute of odour, and are fusible at 158°. Camphoric acid is dibasic; it may be rendered anhydrous by sublimation. A solution of camphoric acid produces a precipitate in a solution of neutral acetate of lead.

It appears that three isomeric modifications of camphoric acid exist: the compound just described is characterized by its power of producing right-handed rotation of a ray of polarized light; but, according to Chautard, the camphoric acid obtained by treating the camphor of the *Matricaria parthenium* with nitric acid, exerts a left-handed rotatory action; and if the right-handed and left-handed camphoric acids be mixed in equivalent proportions, a compound acid is obtained which, like racemic acid, is destitute of any rotatory action upon the plane of polarization: this mixed acid differs somewhat in chemical properties from either of its two components (*Comptes Rendus*, xxxvii. 166).

(1200) *Borneo Camphor* ($C_{20}H_{18}O_2$).—This substance differs from the preceding variety of camphor in containing two equivalents more of hydrogen. It is less fusible and volatile than common camphor, but is denser and harder. It exerts a right-handed rotatory action upon polarized light, but its power in this respect is smaller than that of ordinary camphor, from which it can scarcely be distinguished in taste, smell, solubility, and general appearance. It crystallizes in small, transparent, regular, colourless, six-sided prisms, which melt at 388°, and enter into ebullition at 413°. If gently warmed with nitric acid of moderate strength, it loses two equivalents of hydrogen, and is converted into ordinary camphor.

Borneo camphor occurs in the *Dryobalanops*, in combination with an oil ($C_{20}H_{16}$) termed *borneène*, which has the composition of ordinary turpentine: the same hydrocarbon also occurs in the essential oil of valerian. In order to procure the camphor, punctures are made into the wood of the growing tree, and the oil which exudes is submitted to distillation: the borneène is volatilized, and an imperfect separation of the camphor and oil is thus effected. If borneène be repeatedly distilled with a solution of potash, it combines with two equivalents of water, and is converted into Borneo camphor. A similar conversion into the same camphor also occurs if the oil be dissolved in an equal bulk of an alcoholic solution of potash, and be left at rest in imperfectly closed vessels for a few days; on dilution with water the camphor is separated. Borneo camphor, if mixed with anhydrous phosphoric acid and distilled, loses two equivalents of water, and is reconverted into borneène.

Allusion has already been made to other camphors, such as—

Cubebs camphor (1193)	($C_{30}H_{24}$, 2 HO)
Turpentine camphor (1189) . . .	($C_{20}H_{16}$, 4 HO)
Peppermint camphor (1196) . . .	($C_{20}H_{18}$, 2 HO),

and so on. These compounds, however, are of little importance.

(1201) *b. Indifferent essential Oils containing oxygen.*—The properties of many of these have been already mentioned when speaking of the hydrocarbons with which they are associated (1190—1196).

1. *Oil of Lavender* (*Sp. gr.* 0·898).—The exact composition of this fragrant and well-known oil has not been accurately ascertained. It is soluble in concentrated acetic acid: when long kept it deposits a large proportion of laurel camphor.

2. Oil of wormwood is isomeric with laurel camphor.

Besides these, there are a great variety of essences which contain oxygen, but which have been but imperfectly examined; such, for instance, as the oils of cajeput, of dill, of marjoram, of pennyroyal, of sage, of sassafras, and of many other plants.

(1202) *c. Oils analogous to the Aldehyds.*—The oils of bitter almonds, of spiræa, of cinnamon, and of cummin, are characterized by forming crystallized compounds with bisulphite of soda, and, like the aldehyds of the series homologous with ordinary alcohol, they exhibit a strong tendency to form acids by the absorption of two equivalents of oxygen. The oils of this class, however, differ from the ordinary aldehyds in the facility with which they allow the displacement of one equivalent of the hydrogen which they contain by an equivalent of chlorine, of sulphur, of cyanogen, and of various electro-negative elements. They have been regarded as hydrides of peculiar oxidized radicles; for example:—

Oil of bitter almonds	$C_{14}H_5O_2, H = Bz, H$	Hydride of benzoyl
Oil of cummin . .	$C_{20}H_{11}O_2, H = Cu, H$	Hydride of cumyl
Oil of cinnamon . .	$C_{18}H_7O_2, H = Ci, H$	Hydride of cinnamyl.

In describing these oils it will be convenient to consider their most important derivatives, which are very numerous, and embrace compounds many of which present several points of interest.

In this section the following compounds will be examined:—

1. Essence of bitter almonds.—Benzoic series.—Hippuric acid.
2. Essence of cummin.—Cuminic series.
3. Essence of cinnamon.—Cinnamic series.—Coumarin.
4. Essence of spiræa.—Salicylic series.—Salicin.
5. Essence of aniseed.—Anisic series.

1. *Essence of Bitter Almonds.—Benzoic Series.*

(1203) The essence of bitter almonds is the most important member of the group of oxidized essential oils. It formed the subject of a remarkable memoir by Liebig and Wöhler (*Ann. de Chimie,* II. li. 273), in which they first systematically applied the theory of compound radicles to substances of organic origin. The publication of this paper exercised an immediate and extraordinary influence upon the study of organic chemistry, in which, indeed, it inaugurated a new era, and thus led to a series of brilliant discoveries which followed in rapid succession.

The following compounds of the benzoic series will be briefly described, or the mode of their formation will be indicated :—

Amygdalin	$(C_{40}H_{27}NO_{22}, 6\,Aq)$
Amygdalic acid	$(HO, C_{40}H_{26}O_{24})$

Hydride of benzoyl	$C_{14}H_5O_2, H$	$=BzH$
Nitro-benzoyl	$C_{14}H_5O_2, NO_4$	$=BzNO_4$
Hydride of chloro-benzoyl	$C_{14}H_5Cl_2, H$	
Chloride of benzoyl	$C_{14}H_5O_2, Cl$	$=BzCl$
Chlorohydride of benzoyl	$(C_{14}H_5O_2, H + C_{14}H_5O_2, Cl$	$=BzH, BzCl$
Sulphide of benzoyl	$C_{14}H_5O_2, S$	$=BzS$
Bromide of do.	$C_{14}H_5O_2, Br$	$=BzBr$
Iodide of do.	$C_{14}H_5O_2, I$	$=BzI$
Cyanide of do.	$C_{14}H_5O_2, C_2N$	$=BzCy$
Formobenzoylic acid	$HO, C_{14}H_6O_2, C_2HO_3$	$=HO, BzH, C_2HO_3$
Benzoate of hydride of benzoyl	$2\,C_{14}H_6O_2, C_{14}H_6O_4$	$=BzH, 2(HO, BzO)$
Hydrocyanate of hydride of benzoyl	$C_{14}H_6O_2, HC_2N$	$=BzH, HCy$
Benzimide (hydride of cyano-benzoyl)	$C_{46}H_{18}N_2O_4$	
Benzoic acid	$HO, C_{14}H_5O_3$	$=HO, BzO$
Benzoic anhydride	$C_{14}H_5O_3, C_{14}H_5O_3$	$=BzO, BzO$
Benzo-acetic anhydride	$C_{14}H_5O_3, C_4H_3O_3$	$=BzO, \overline{O}thO$
Sulphobenzoic acid	$2\,HO, C_{14}H_4S_2O_8$	
Nitrobenzoic acid	$HO, C_{14}H_4NO_4, O_3$	
Benzamic, or amido-benzoic acid	$HO, C_{14}H_4, H_2N, O_3$	

Benzamide . . .	$H_2N, C_{14}H_5O_2$	$= H_2N, Bz$
Benzanilide . .	$C_{12}H_5, HN, C_{14}H_5O_2$	$= C_{12}H_5, HN, Bz$
Hydrobenzamide .	$C_{42}H_{18}N_2$	
Dibenzoylimide .	$C_{28}H_{11}NO_4$	
Benzhydramide .	$C_{44}H_{18}N_2O_2$	
Benzoylic azotide .	$C_{30}H_{12}N_2$	
Azobenzoyl . .	$C_{42}H_{15}N_2$	
Benzoic alcohol .	$C_{14}H_7O, HO$	
Benzo-ether . .	$C_{14}H_7O, C_{14}H_7O$	
Toluidine . . .	$C_{14}H_7, H_2N$	

Benzoine . . .	$C_{28}H_{12}O_4$	$= C_{28}H_{11}O_4, H$
Benzile	$C_{28}H_{10}O_4$	
Benzilic acid . .	$HO, C_{28}H_{11}O_5$	$= HO, C_{28}H_{11}O_4, O$
Chloride of benzile	$C_{28}H_{11}O_4Cl$	$= C_{28}H_{11}O_4, Cl$
Benzoinamide . .	$C_{84}H_{36}N_4$	
Benzoinam . . .	$C_{56}H_{24}N_2O_2$	

(1204) *Amygdalin* ($C_{40}H_{27}NO_{22}, 6Aq$).—The pulp of the bitter almond contains a large portion of a bland, nearly tasteless, colourless fixed oil which can be separated from it by pressure, and which is identical in properties with that furnished by the sweet almond; but the kernel does not contain any essential oil ready formed. As soon, however, as the pulp is bruised and moistened with water, the fragrant odour of the essence is perceived. This development of the essential oil is due to the decomposition of *amygdalin*, a crystallizable azotized principle which is contained in the kernel, in addition to the oily, starchy, saccharine, and ligneous constituents of the seed.

In order to extract the amygdalin, the cake which remains after the fixed oil has been separated by expression is broken into fragments, and digested with hot alcohol of sp. gr. 0·825. The solution must be filtered, and the alcohol distilled off; the syrupy residue must then be diluted with water, mixed with yeast, and set aside to ferment, in order to decompose the sugar; and on filtering the liquid and evaporating, the amygdalin crystallizes in acicular tufts. It is very soluble in water, from which it is deposited in prisms with 6 equivalents of water. The whole of this water is expelled by a temperature below 250°.

Amygdalin has a sweetish, somewhat bitter taste, and is not poisonous. Its solution exerts a left-handed rotation upon a ray of polarized light. When it is treated with alkaline solutions, ammonia is expelled, and a new acid, the *amygdalic* ($HO, C_{40}H_{26}O_{24}$), is found in the liquid; this decomposition is analogous to that produced in asparagin under similar circumstances:—

$$\overbrace{C_{40}H_{27}NO_{22}}^{\text{Amygdalin.}} + KO, HO + HO = \overbrace{KO, C_{40}H_{26}O_{24}}^{\text{Amygdalate of Potash.}} + H_3N.$$

The most remarkable change, however, to which amygdalin is subject, is that which it undergoes when the bruised kernel in which it is contained is brought into contact with water. As soon as this is done, the peculiar and agreeable odour of bitter almonds is perceived; in twenty-four hours all traces of amygdalin will have disappeared, and in its place an essential oil, hydrocyanic acid, sugar, and formic acid, will be found. This singular transformation is the result of a species of fermentation produced by the action of a peculiar azotised matter which resembles the diastase of malt, to which the name *synaptase*, or *emulsin*, has been given. This ferment is contained both in the bitter and the sweet almond. If boiling water be poured upon the pulp, the synaptase is coagulated, and no formation of the essence ensues. In preparing the essence cold water should therefore be employed, and the mixture should be allowed to stand for some hours before proceeding to distillation.*

The change which occurs in amygdalin under the influence of synaptase may be thus represented:—

$$\overbrace{2\,(C_{40}H_{27}NO_{22})}^{\text{Amygdalin.}} = \overbrace{4\,(C_{14}H_5O_2, H)}^{\text{Essential Oil.}} + \overbrace{2\,(H, C_2N)}^{\text{Hydrocy. Acid.}} + \overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}$$

$$+ \overbrace{4\,(HO,C_2HO_3)}^{\text{Formic Acid.}} + 6\,HO.$$

100 parts of amygdalin yield about 41 of the essential oil, and 6 of hydrocyanic acid.

The proportion of hydrocyanic acid liberated by the reaction is perfectly definite, and it has been proposed by Liebig and Wöhler to take advantage of this fact in prescribing hydrocyanic acid medicinally. Amygdalin may be dissolved in water, and it may be kept unchanged; but if it be mixed with an emulsion of sweet almonds, decomposition commences immediately, and the characteristic odour of the essence is developed. Seventeen grains of amygdalin when dissolved in one ounce of emulsion of sweet almonds, would furnish exactly one grain of pure hydrocyanic acid; or it would contain an amount of the acid equivalent to 50 minims of the dilute hydrocyanic acid of the London Pharmacopœia.

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* Synaptase is a ferment which may be advantageously applied to many organic compounds in order to effect their transformation into new products. It may be procured from the cake left after the expression of the oil of the sweet almond. This mass must be diffused through a quantity of pure water equal to about thrice its weight; the liquid must be strained through a cloth, and the undissolved portion submitted to pressure. The emulsion thus procured must be left for three or four days at a temperature of 70° or 80°, during which time it becomes separated into two layers; the upper one consisting of a curd-like coagulum, and the lower one forming a clear liquid, like whey. In the course of two or three days this lower stratum ceases to yield any precipitate on the addition of acetic acid: when this point has been reached, alcohol must be added so long as it occasions a precipitate. This precipitate consists of synaptase in combination with phosphates of lime and

(1205) Essence of Bitter Almonds.—*Hydride of Benzoyl* ($C_{14}H_5O_2, H$); *Sp. gr.* 1·043.—In order to extract this essence, the bitter almond cake which is left after the expression of the fixed oil is crushed and made into a thin cream with water. It is then introduced into a still, where it is allowed to remain for twenty-four hours, with occasional agitation, in order that the amygdalin may be completely decomposed. At the end of that time the distillation is proceeded with. This operation is best effected by the injection of steam; the liquid is thus speedily raised to the boiling point, and all risk of charring the vegetable matter is averted: the oil passes over as usual with the vapour, and may be condensed in suitable receivers. The distillation must be continued so long as the distillate comes over with a milky appearance.

A considerable quantity of the essence is dissolved in the distilled water, but most of this can be recovered by subjecting the water to a second distillation, the essence coming over with the first portions. The kernels of the peach, the plum, the cherry, and other stone fruit, as well as the leaves of the laurel (*Prunus laurocerasus*) also yield this essence in notable quantities.

The crude essence, in addition to hydride of benzoyl, contains hydrocyanic and benzoic acid, and a crystalline body termed benzoin (1212): it is extremely poisonous, owing to the presence of hydrocyanic acid; but it may be readily purified from the latter

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magnesia: it must be washed with absolute alcohol, and dried *in vacuo* over sulphuric acid.

The synaptase thus obtained cannot be freed from the salts which accompany it, but it is sufficiently pure to enable its action as a ferment to be studied. When dried as directed, it may be preserved unaltered: but if left in a moist condition, it speedily becomes putrid. It is completely soluble in cold water; the liquid has an acid reaction, which enables it to hold the earthy phosphates in solution. In this state it speedily transforms amygdalin into the essence of bitter almonds and other products. The aqueous solution of synaptase becomes turbid when heated, owing to the separation of a portion of the earthy phosphates; the liquid, however, again becomes clear as it cools, but no longer possesses the power of effecting the transformation of amygdalin into hydride of benzoyl. A solution of synaptase is entirely precipitated by [illegible] of gall, and the precipitate so obtained acts upon amygdalin in [illegible] as synaptase itself.

compound by agitating the oil briskly with a mixture of milk of lime and protochloride of iron, and then submitting it to distillation.

The purified oil is not poisonous. It is inflammable, and burns with a smoky flame; when heated to 356° it boils, and may be distilled unaltered. Hydride of benzoyl is soluble in 30 parts of water, but it is dissolved by alcohol and by ether in all proportions. This oil exerts no rotatory action upon polarized light.

When essential oil of bitter almonds, either in its pure or its rectified condition, is left in contact with the atmosphere and with water, it gradually absorbs oxygen, and is at length wholly converted into a crystalline mass consisting of benzoic acid :—

$$\overbrace{C_{12}H_5O_2,\ H}^{\text{Hydride of Benzoyl.}} + O_2 = \overbrace{HO,\ C_{14}H_5O_2,\ O}^{\text{Benzoic Acid.}}.$$

When oil of bitter almonds is heated with hydrate of potash, it yields hydrogen and the benzoate of the alkali :—

$$\overbrace{C_{14}H_5O_2,\ H}^{\text{Hydride of Benzoyl.}} + KO,\ HO = \overbrace{KO,\ C_{14}H_5O_3}^{\text{Benzoate of Potash.}} + 2\ H.$$

Concentrated nitric acid converts the essence into nitro-benzoic acid ($HO, C_{14}H_4, NO_4, O_3$), with brisk evolution of heat; but if the reaction be moderated by the addition of water, a yellowish oil is formed, which gradually solidifies; it is a compound in which the hydrogen of the hydride has been displaced by peroxide of nitrogen :—

$$\overbrace{C_{14}H_5O_2,\ H}^{\text{Hydride of Benzoyl.}} + HO,\ NO_5 = \overbrace{C_{14}H_5O_2,\ NO_4}^{\text{Nitro-benzoyl.}} + 2\ HO.$$

When oil of bitter almonds is treated with perchloride of phosphorus, it yields a compound termed *chlorobenzole*, or *hydride of chlorobenzoyl* ($C_{14}H_5Cl_2, H$), in which the oxygen of the essence appears to have been displaced by chlorine, whilst oxychloride of phosphorus is formed, and can be expelled by heat. Chlorobenzole is a limpid, colourless liquid, of sp. gr. 1·245; its density in the form of vapour is 5·625. It has but little odour at ordinary temperatures, but when heated it gives off an irritating vapour. Chlorobenzole boils at 403°. It is insoluble in water, but readily soluble in alcohol and in ether.

(1206) *Chloride of Benzoyl, Benzoic Oxychloride* ($C_{14}H_5O_2, Cl$); *Sp. gr. of liquid* 1·196, Liebig and Wöhler; 1.25, Cahours; *of vapour* 4·987.—When a current of dry chlorine is transmitted through the essential oil of bitter almonds gently warmed, much hydrochloric acid is evolved, and chloride of benzoyl is obtained in the form of a colourless liquid, the vapour of which produces lachrymation; it has a peculiar irritating odour resembling that of horseradish.

Chloride of benzoyl boils at 383°, and burns with a green smoky flame. This substance sinks in water without mixing with it; but if boiled with water, it is gradually dissolved, and decomposed into hydrochloric and benzoic acids; $C_{14}H_5O_2,Cl + 2HO = HO,C_{14}H_5O_3 + HCl$.

The best method of preparing the chloride of benzoyl, when required in considerable quantity, consists in heating gently in a retort a mixture of 122 parts of crystallized benzoic acid, and 211 of perchloride of phosphorus (1 equivalent of each substance): a violent reaction occurs, attended with a copious extrication of hydrochloric acid:—

$$\overbrace{HO,\ C_{14}H_5O_3}^{\text{Benzoic Acid.}} + PCl_5 = \overbrace{C_{14}H_5O_2,\ Cl}^{\text{Chlor. Benzoyl.}} + HCl + \overbrace{PO_2Cl_3}^{\text{Oxychlor. Phosph.}};$$

when this has terminated, the mixture is submitted to distillation. As soon as the boiling point rises to 383°, pure chloride of benzoyl passes over, the portions which distil at a lower point consisting of a mixture of oxychloride of phosphorus and chloride of benzoyl. This mixture may be purified by distilling it from anhydrous benzoate of soda, the oxychloride of phosphorus becoming decomposed in the following manner:—

$$\overbrace{3(NaO,\ C_{14}H_5O_3)}^{\text{Benzoate of Soda.}} + \overbrace{PO_2Cl_3}^{\text{Oxychlor. Phosph.}} = \overbrace{3(C_{14}H_5O_2,Cl)}^{\text{Chloride of Benzoyl.}} + \overbrace{3\ NaO,\ PO_5}^{\text{Phosph. Soda.}}.$$

Chloride of benzoyl has been extensively employed by Gerhardt in the preparation of the anhydrides of the organic acids (1099).

Gaseous ammonia decomposes it, and yields benzamide (1054), and hydrochlorate of ammonia:—

$$\overbrace{C_{14}H_5O_2,\ Cl}^{\text{Chlor. Benzoyl.}} + 2\ H_3N = H_4NCl + \overbrace{H_2N,\ C_{14}H_5O_2}^{\text{Benzamide.}}.$$

Aniline attacks it in a similar manner, and produces benzanilide ($C_{12}H_5$, HN, $C_{14}H_5O_2$). When mixed with alcohol it yields benzoic ether:—

$$\overbrace{C_{14}H_5O_2,\ Cl}^{\text{Chlor. Benzoyl.}} + \overbrace{C_4H_5O,\ HO}^{\text{Alcohol.}} = \overbrace{C_4H_5O,\ C_{14}H_5O_3}^{\text{Benzoic Ether.}} + HCl.$$

Sometimes in the reaction of chlorine upon the hydride of benzoyl, brilliant colourless plates of a substance sparingly soluble in cold alcohol are deposited. They are formed by a combination of chloride with hydride of benzoyl ($C_{14}H_5O_2H$, $C_{14}H_5O_2$, Cl), which is termed *chlorohydride of benzoyl.*

Sulphide of Benzoyl 2 ($C_{14}H_5O_2$,S).—When chloride of benzoyl is distilled with sulphide of lead, a yellowish oil of the above composition passes over; it gradually forms a yellow crystalline mass, which has a disagreeable sulphurous odour.

A *bromide* of benzoyl ($C_{14}H_5O_2$, Br), and an *iodide* ($C_{14}H_5O_2$, I) may be obtained by analogous methods.

Cyanide of benzoyl ($C_{14}H_5O_2$, Cy) may be obtained in a similar manner, in the form of a yellow oil, by distilling the chloride of benzoyl with cyanide of mercury.

(1207) *Formobenzoylic* or *Mandelic Acid* (HO, $C_{14}H_6O_2$, C_2HO_3).—When the distilled water of bitter almonds, (containing hydrocyanic acid, and the essential oil) is boiled with hydrochloric acid, a curious reaction occurs; the hydrocyanic acid is decomposed into ammonia which unites with the hydrochloric acid, and formic acid which enters into combination with the oil of almonds, producing a new body possessed of acid properties and termed *formo-benzoylic* acid:—

$$\overbrace{C_{14}H_6O_2}^{\text{Hydr. of Benzoyl.}}+HCl+4\ HO+\overbrace{H,C_2N}^{\text{Hydrocy. Acid.}}=H_4NCl+\overbrace{HO,\ C_{14}H_6O_2,C_2HO_3}^{\text{Formobenzoylic Acid.}}.$$

On evaporating the solution, the acid may be obtained in mixture with hydrochlorate of ammonia, from which it may be separated by ether; the ethereal solution deposits it in rhomboidal tables. It has a sour taste, and is easily soluble in alcohol. When heated, it fuses at a low temperature, emitting an agreeable odour of hawthorn blossoms. Formobenzoylic acid is also obtained by dissolving amygdalin in concentrated hydrochloric acid. Formobenzoylic acid furnishes one of the best instances of the class of colligated acids, in which the saturating power of the original acid, the formic, remains unimpaired by its union with the colligate. It forms soluble crystallizable salts with baryta and silver, and with other bases.

A compound of *benzoic acid with hydride of benzoyl* [2 ($C_{14}H_5O_2$,H) $C_{14}H_6O_4$] ? is obtained by acting upon the moist essence of bitter almonds with undried chlorine gas; 3 equivalents of the essence concur to its formation, but 1 equivalent only has undergone oxidation; $3\ (C_{14}H_6O_2)+2\ HO+Cl=HCl+(2\ C_{14}H_6O_2,\ C_{14}H_6O_4)$. This reaction presents a certain analogy with that by which acetal (973) is formed. The benzoic hydride of benzoyl is insoluble in water, but it crystallizes from its alcoholic solution in square prisms, which may be fused at a gentle heat and volatilized without decomposition: it presents none of the characters of an acid. An alcoholic solution of potash gradually decomposes it, and crystals of benzoate of potash are deposited. It appears that under certain circumstances 3 equivalents of the essence combine with 1 of benzoic acid (Laurent and Gerhardt), but the composition of this body is somewhat uncertain.

Hydrocyanate of Hydride of Benzoyl.—If the mixture of hydrochloric acid and the distilled water of bitter almonds be evaporated at a gentle heat, without boiling, a yellow oily liquid of sp. gr. 1·124 is formed; this substance is sparingly soluble in water, but freely so in alcohol and ether. Voelckel states it to be a compound of hydrocyanic acid with hydride of benzoyl ($C_{14}H_6O_2$, HC_2N) : it is decomposed into its two components by a temperature of 338°.

The substance to which the name of *benzimide* ($C_{46}H_{18}N_2O_4$)* was given by Laurent, is the result of the action of hydrocyanic acid upon the essence. If the hydride of benzoyl be mixed with a fourth of its bulk of anhydrous hydrocyanic acid, and gently warmed after agitation with an alcoholic solution of potash, white curdy flocculi of *hydride of cyanobenzoyl* (benzimide) are deposited. The same substance is also sometimes met with in the resinous residue of the distillation of the crude essence; and on treating this with boiling alcohol, benzimide is deposited in white flocculi as the liquid cools. Benzimide is sparingly soluble in alcohol and in ether. It fuses on the application of heat, and at a high temperature is decomposed, leaving a carbonaceous residue; fuming sulphuric acid dissolves it with a blue colour, which fades on dilution.

(1208) BENZOIC ACID (HO, $C_{14}H_5O_3$) *Sp. gr. of vapour* 4·27.—Benzoic acid occurs abundantly in the balsamiferous plants, independently of its artificial origin from bitter almond oil already mentioned.

Gum Benzoin, the produce of the *Styrax Benzoin* of the Asiatic archipelago, is the principal source of the supply of benzoic acid. Common benzoin occurs in reddish lumps which sometimes have a lamellated fracture, and contain whitish opaque masses. When recent it emits an odour of bitter almonds. Gum benzoin appears to be composed of a mixture of three varieties of resin, with benzoic acid and a small quantity of a fragrant essential oil. Only one of the resins is soluble in ether, a second is soluble in alcohol only. The white opaque masses appear to consist of the resin which is soluble in ether; they yield less benzoic acid than the brown portions.

Preparation.—Benzoic acid may be extracted from powdered benzoin by boiling it for some hours with milk of lime, filtering the solution of benzoate of lime from the insoluble compound of resin and lime, and, after concentrating the filtrate, adding hydrochloric acid; benzoic acid is thus precipitated, and may be purified by sublimation. The acid is, however, generally extracted by the less economical but simpler process of direct sublimation from gum benzoin, which contains 14 or 15 per cent. of the acid: if the resin be coarsely powdered and exposed to a temperature of about 300°, the acid which exists ready formed in it is expelled, and may be condensed in suitable receivers. Mohr's plan of conducting the sublimation, which has been already described when speaking of the preparation of pyrogallic acid (1124) is the simplest and best method. The resins of tolu and of benzoin when treated with boiling nitric acid yield an amorphous form of benzoic acid, which is coloured yellow with a resinous matter which accompanies it into its salts, and hinders them from crystallizing: balsam of tolu often yields nearly half its weight of this acid. This resinous acid is completely soluble in boiling water; when this form of the acid is exposed to the sun's rays it becomes covered with white crystals of pure benzoic acid; and when sublimed the ordinary crystalline acid is obtained.

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* Laurent finds the formula ($C_{28}H_{11}NO_4$) originally given by him for this compound to have been erroneous.

Properties.—Benzoic acid assumes the form of white, glistening, extremely light, flexible needles, which usually have an agreeable aromatic odour, and a hot bitterish taste. The odour, however, is not due to the acid, but to the presence of a trace of essential oil which accompanies the acid during the sublimation. Benzoic acid melts at 248°; it sublimes at 293°, and boils at 462°. Its vapours are acrid and irritating, when kindled in the open air they burn with a smoky flame. The acid requires about 200 parts of cold water, and 25 of boiling water, for its solution; but it is readily dissolved by alcohol and by ether.

Benzoates.—Most of the benzoates are soluble in water, and in alcohol. If a strong acid, such as the sulphuric or hydrochloric, be added to their aqueous solutions, a crystalline precipitate of benzoic acid is deposited. Potash and ammonia form both neutral and acid salts with benzoic acid. *Neutral benzoate of potash* ($KO, C_{14}H_5O_3 + Aq$) crystallizes with difficulty in penniform crystals, which creep up the sides of the vessel during their formation. The *acid salt of potash* ($KO, HO, 2\ C_{14}H_5O_3$), may be obtained from its solution in alcohol, in colourless, pearly tables, which are sparingly soluble in water. It is obtained as a secondary product in the preparation of acetic anhydride by decomposing acetate of potash with chloride of benzoyl. Neutral benzoate of *ammonia* is very soluble in water. It is sometimes used as a means of separating iron from nickel and cobalt. The benzoate of *peroxide of iron* falls as a bulky brownish-white gelatinous mass when a neutral solution of a persalt of iron is mixed with one of benzoate of ammonia: perbenzoate of iron is soluble in alcohol. The benzoates of *yttria, zirconia, tin,* and *lead,* are insoluble in water; that of *silver* is sparingly soluble in boiling water. A neutral solution of a persalt of iron may be used for detecting the presence of benzoic acid in solution. When any of the benzoates are treated with phosphoric acid, benzoic acid is sublimed, and may be recognised by its characteristic odour. The benzoates of the alkalies and of the earths when submitted to destructive distillation yield a particular hydrocarbon termed *benzole* or *benzine* ($C_{12}H_6$), and a compound termed *benzophenone* ($C_{12}H_5, C_{14}H_5O_2$); these substances are intimately related to the *phenic* group of compounds which will be described in the chapter upon the products of destructive distillation. When benzoate of lime and formiate of lime are distilled in the proportion of one equivalent of each, hydride of benzoyl is the result (Piria):—*

$$\overbrace{CaO, C_{14}H_5O_3}^{\text{Benzoate of Lime.}} + \overbrace{CaO, C_2HO_3}^{\text{Formiate of Lime.}} = 2(CaO, CO_2) + \overbrace{C_{14}H_6O_2}^{\text{Hydride of Benzoyl.}}.$$

Benzoic acid is dissolved by oil of vitriol, and is precipitated unchanged on dilution with water; but fuming sulphuric acid converts it into a dibasic compound acid, the *sulphobenzoic* ($2\,HO, C_{14}H_4S_2O_8$). Fuming nitric acid converts the benzoic into *nitrobenzoic acid* ($HO, C_{14}H_4NO_4,O_3$); and a mixture of oil of vitriol and nitric acid produces *dinitrobenzoic acid* ($HO, C_{14}H_3, 2\,NO_4, O_3$). Chlorine produces not less than three chlorinated acids: viz., *monochlorinated, dichlorinated* and *trichlorinated* benzoic acid, in which 1 equivalent, 2 equivalents, and 3 equivalents of hydrogen respectively are displaced by a corresponding number of equivalents of chlorine. When benzoic acid is treated with perchloride of phosphorus it yields chloride of benzoyl in abundance (1206).

Benzoic anhydride ($C_{14}H_5O_3, C_{14}H_5O_3$).—This compound is obtained by decomposing anhydrous benzoate of soda with chloride of benzoyl, or with oxychloride of phosphorus (1099). The result of the reaction is washed with water weakly alkalized with carbonate of soda: benzoic anhydride is left in the form of a white mass insoluble in water, but soluble in ether and in hot anhydrous alcohol, from which it crystallizes in oblique prisms. It melts at about 108° F., and may be distilled unaltered at 590°. Boiling water slowly converts it into the hydrated acid; the change is hastened by the addition of an alkali. It enters into the formation of many double anhydrides (1100): such, for example, as *benzoacetic anhydride* ($C_{14}H_5O_3$, $C_4H_3O_3$) which is obtained by heating acetic oxychloride ($C_4H_3O_2Cl$) with dried benzoate of soda. A brisk reaction occurs at ordinary temperatures; when this is over the residue must be washed with water, and with a weak solution of carbonate of soda: benzoacetic anhydride is left in the form of a neutral oil which is heavier than water, and emits an agreeable odour of sherry wine. Boiling water slowly decomposes it into a mixture of acetic and benzoic acids; but the solutions of the alkalies or of their carbonates quickly convert it into acetate and benzoate of the base. It cannot be distilled without experiencing decomposition: acetic anhydride passes over first, and if the distillation be stopped as soon as the temperature of the boiling liquid reaches 536°, the residue in the retort solidifies on cooling into a mass of crystallized benzoic anhydride.

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* Piria finds that cinnamic, cuminic, and other aldehyds may be obtained by distilling the salts of their corresponding acids with formiate of lime. Thus a mixture of cinnamate and formiate of lime yields oil of cinnamon.

(1209) *Benzamic acid; Carbanilic acid* or *Amido-benzoic acid* ($C_{14}H_7NO_4 = HO, C_{14}H_4, H_2N, O_3$) as it is more appropriately termed, is not a true amidated acid (1047), but benzoic acid in which an equivalent of hydrogen has been displaced by an equivalent of amidogen. It is isomeric with anthranilic acid (1287) and is obtained by the action of reducing agents upon nitrobenzoic acid. If an alcoholic solution of nitro-benzoic acid be saturated with ammonia and with sulphuretted hydrogen, and then boiled, it becomes green, and a copious deposit of sulphur occurs: this operation must be repeated two or three times, in order to complete the decomposition of the nitrobenzoic acid:—

$$\overbrace{HO, C_{14}H_4, NO_4, O_3}^{\text{Nitrobenzoic Acid.}} + 6\,HS = \overbrace{HO, C_{14}H_4(H_2N)_2O_3}^{\text{Amidobenzoic Acid.}} + 4\,HO + 6\,S.$$

The liquid must be evaporated to the consistence of syrup, supersaturated with acetic acid, and the precipitate drained upon porous tiles. It must then be redissolved in boiling water; the solution digested with animal charcoal, filtered, and allowed to crystallize. Amido-benzoic acid crystallizes in radiated tufts of delicate needles, which are readily soluble in alcohol and in ether. It has a sweet, sourish taste, but no odour. It forms an insoluble green precipitate when mixed with salts of copper; with salts of silver it gives a white curdy precipitate, which if left in the liquid becomes crystalline.

This acid likewise possesses the property of combining with other acids. Oil of vitriol dissolves amido-benzoic acid by the aid of heat, and on cooling, it deposits brilliant crystals, ($C_{14}H_7NO_4$, HO, SO_3, 2 Aq), which may be recrystallized from boiling water or from alcohol: their aqueous solution has an extremely sweet taste. A similar compound ($C_{14}H_7NO_4$, HO, NO_5) may be formed with nitric acid.

By the action of reducing agents upon dinitro-benzoic acid, a compound, ($C_{14}H_8N_2O_4$,) analogous to the amido-benzoic acid, having the composition of *diamidobenzoic acid*, HO, $C_{14}H_3(H_2N)_2O_3$, has been obtained (Voit), but it possesses none of the characters of an acid; it combines readily with acids, the introduction of the second equivalent of amidogen having given it a decided basic energy.

(1210) *Action of Ammonia on the Oil of Bitter Almonds.*—Several compounds are produced by the action of ammonia upon this essence, which are different according as the essence employed is pure, or contains hydrocyanic acid. If it be pure, hydrobenzamide and dibenzoylimide are the result of the reaction: if it be in the crude state, the hydrocyanic acid takes part in the reaction, and benzhydramide and benzoylic azotide are formed.

1. *Hydrobenzamide* ($C_{42}H_{18}N_2$) is the most interesting of these compounds; it may be formed by simply agitating the oil with a solution of ammonia, and afterwards leaving it at rest for some days at the ordinary temperature: but the reaction is completed in a few hours if the mixture be heated to the boiling point. In either case the mixed liquids gradually become converted into a crystalline mass of hydrobenzamide, which must be washed with ether and crystallized from boiling alcohol:—

$$3\,\overbrace{(C_{14}H_6O_2)}^{\text{Hydr. Benzoyl.}} + 2\,H_3N = \overbrace{C_{42}H_{18}N_2}^{\text{Hydrobenzamide.}} + 6\,HO.$$

Hydrobenzamide forms colourless octohedra with a rhombic base. It is destitute of odour, and insoluble in water, but readily soluble in ether. It melts at 230°; and, if heated for some time to about 260°, or if boiled with a solution of potash, it is converted into the isomeric base termed amarine or benzoline (1068).

When hydrobenzamide is fused with potash, several new compounds are formed, such as *benzostilbine* ($C_{31}H_{11}O_2$), and *benzolone* ($C_{11}H_4O$), whilst the nitrogen is expelled in the form of ammonia.

Hydrobenzamide, when boiled with hydrochloric acid, is decomposed; sal ammoniac is formed, and hydride of benzoyl is set at liberty. A similar change is also produced by mere boiling of its alcoholic solution, but the ammonia in that case is liberated in the uncombined form.

2. *Dibenzoylimide*($C_{28}H_{13}NO_2$)is obtained by passing ammoniacal gas into an alcoholic solution of essential oil of bitter almonds. It is gradually separated in the form of a resinous mass which is soluble in boiling alcohol, and from which it is deposited as a yellowish powder composed of brilliant feathery crystals (Robson).

$$2\ \overbrace{(C_{14}H_6O_2)}^{\text{Hydr. Benzoyl.}} + H_3N = \overbrace{C_{28}H_{13}NO_2}^{\text{Dibenzoylimide.}} + 2\ HO.$$

3. *Benzhydramide*, or *Hydride of Cyanazobenzoyl a*,—($C_{44}H_{18}N_2O_2$) was originally stated by Laurent to be isomeric with hydrobenzamide, but when he re-examined this substance conjointly with Gerhardt, this statement was ascertained to be an error. If the crude essence of bitter almonds be heated to 212°, and saturated with ammonia, then dissolved in a mixture of alcohol and ether and left to itself for three or four days, a deposit is formed which consists of two portions, viz. *benzhydramide*, and *benzoylic azotide*: they may be separated by the action of boiling alcohol. Benzhydramide is soluble in boiling alcohol, from which on cooling and spontaneous evaporation it is deposited in small brilliant needles, which are freely soluble in ether; and which, when boiled with hydrochloric acid, are decomposed into hydrocyanic acid, hydrochlorate of ammonia, and hydride of benzoyl.

4. The portion which is left undissolved by alcohol is the *benzoylic azotide* of Laurent. It is in the form of a white crystalline powder, which is nearly insoluble in alcohol and in ether: it fuses on the application of heat, and crystallizes on cooling.

The formation of these two compounds is explained by the following equations:—

$$\overbrace{3\ (C_{14}H_6O_2)}^{\text{Hydride of Benzoyl.}} + \overbrace{H, C_2N}^{\text{Hydrocy. acid.}} + H_3N = \overbrace{C_{44}H_{18}N_2O_2}^{\text{Benzhydramide.}} + 4\ HO;$$

$$2\ (C_{14}H_6O_2) + H, C_2N + H_3N = \overbrace{C_{30}H_{12}N_2}^{\text{Benzoylic Azotide.}} + 4\ HO.$$

5. *Azobenzoyl* ($C_{42}H_{15}N_2$) is a third substance which was obtained by Laurent. It is nearly insoluble in alcohol, but soluble in ether: on the application of heat it fuses into a transparent mass, resembling gum in appearance.

(1211) *Alcohol of the Benzoic Series* ($C_{14}H_7O, HO$; Cannizzaro)

Sp. gr. of liquid 1·059; *of vapour* 3·84.—In order to obtain this compound the following process is adopted:—Oil of bitter almonds is dissolved in its own volume of alcohol, and this liquid is mixed with three or four times its bulk of an alcoholic solution of hydrate of potash (of sp. gr. 1·020): a considerable evolution of heat occurs, and a copious deposition of crystals of benzoate of potash takes place: when this reaction has terminated, boiling water is added to the liquid in quantity sufficient to dissolve the benzoate. The greater part of the alcohol must then be distilled off, and more water added to dissolve the benzoate if necessary; the turbid liquid thus obtained must be agitated with ether, and the ethereal layer which separates on standing, must be drawn off and subjected to distillation. The first portions consist of ether, but subsequently pure benzoic alcohol passes over. The reaction of the potash upon the hydride of benzoyl may be thus represented:—

$$2\ \overbrace{(C_{14}H_6O_2)}^{\text{Hydride of Benzoyl.}} + KO, HO = \overbrace{KO, C_{14}H_5O_3}^{\text{Benzoate of Potash.}} + \overbrace{HO, C_{14}H_7O.}^{\text{Benzoic Alcohol.}}$$

Benzoic alcohol is a colourless oily liquid which boils at 400°. It is readily converted by nitric acid at a gentle heat into oil of bitter almonds; and is transformed by chromic acid into benzoic acid: both of these products are the results of oxidation, which may be thus represented:—

$$\overbrace{C_{14}H_8O_2}^{\text{Benzoic Alcohol.}} + O_2 = \overbrace{C_{14}H_6O_2}^{\text{Oil of Bitter Almonds.}} + 2\ HO;\ \text{and}$$

$$C_{14}H_8O_2 + O_4 = \overbrace{HO, C_{14}H_5O_3}^{\text{Benzoic Acid.}} + 2\ HO.$$

It is obvious that oil of bitter almonds and benzoic acid stand in the same relation to benzoic alcohol, that aldehyd and acetic acid do to ordinary alcohol (*vide* Table, p. 430).

If benzoic alcohol be distilled from hydrate of potash, it is decomposed into benzoate of potash and the hydrocarbon known as toluole, which corresponds to olefiant gas in the alcohol series:—

$$3\ \overbrace{(C_{14}H_8O_2)}^{\text{Benzoic Alcohol.}} + KO, HO = \overbrace{KO, C_{14}H_5O_3}^{\text{Benz. Potash.}} + 2\overbrace{(C_{14}H_8)}^{\text{Toluole.}} + 4\ HO.$$

Benzoic alcohol may be made to yield a series of ethers, among which are the following:—

		Boiling point.
Benzo-ether	$C_{14}H_7O, C_{14}H_7O$	about 590°
Benzo-hydrochloric ether .	$C_{14}H_7Cl$	about 360°
Benzo-acetic ether . . .	$C_{14}H_7O, C_4H_3O_3$	410°
Benzo-benzoic ether . . .	$C_{14}H_7O, C_{14}H_5O_3$	653°

Benzo-ether is obtained by heating benzoic alcohol with anhydrous boracic acid in a closed vessel to about 250° for some hours. The boracic acid must then be extracted with boiling water and a weak solution of carbonate of soda, and the residue must be distilled at a temperature of about 590°; benzo-ether passes over, and a hydrocarbon ($C_{28}H_{12}$) remains in the retort:—

$$4\,\overbrace{(C_{14}H_8O_2)}^{\text{Benzoic Alcohol.}} = 2\,\overbrace{(C_{14}H_7O)}^{\text{Benzo-Ether.}} + C_{28}H_{12} + 6\,HO.$$

Benzo-hydrochloric ether when heated in a sealed tube with ammonia furnishes the volatile base *toluidine*, $C_{14}H_7N$, which corresponds to ethylia in the ethylic series. When benzoic alcohol is mixed with oil of vitriol, it yields a compound acid ($HO, C_{14}H_7O, S_2O_6$), corresponding to the sulphethylic. It may be obtained in crystalline plates.

(1212) BENZOINE ($C_{28}H_{12}O_4$).—It has been already mentioned that when the vapour of hydride of benzoyl is transmitted over heated hydrate of potash, benzoate of potash and hydrogen are produced: but if the crude essence be agitated with its own bulk of a saturated alcoholic solution of potash, the oil is slowly changed into a mass of crystals, which are isomeric with the hydride of benzoyl: the same change occurs if the pure hydride be digested with an alcoholic solution of cyanide of potassium: to the substance thus formed the name of *benzoine* has been given. The presence of hydrocyanic acid is necessary to the production of this metamorphosis; but the mode in which it acts is entirely unknown, since it remains in the liquid, unaltered in amount, after the change has been effected.

Benzoine may be obtained in a state of purity by crystallizing it from boiling alcohol, in which it is readily soluble. Ether also dissolves it freely. It is nearly insoluble in cold water, but is somewhat soluble in boiling water. Benzoine is destitute of odour and of taste: at 248° it fuses, and at a higher temperature it may be distilled unaltered. If its vapour be transmitted through red-hot tubes, it is re-converted into the essential oil of bitter almonds. Cold sulphuric acid dissolves it with the production of a violet colour. Benzoine has been regarded as ($C_{28}H_{11}O_4$, H), or as the hydride of a new radicle *stilbyl* ($C_{28}H_{11}O_4$), but the series to which it gives rise has been hitherto but incompletely investigated. When benzoine is fused with hydrate of potash, it becomes converted into benzoate of that base with evolution of hydrogen: but if it be boiled with an alcoholic solution of potash, a beautiful violet-coloured solution is formed which is gradually bleached by boiling, whilst hydrogen is disengaged, and *benzilic acid* remains in combination with the potash:—

$$\overbrace{C_{28}H_{12}O_4}^{\text{Benzoine.}} + KO, HO = \overbrace{KO, C_{28}H_{11}O_5}^{\text{Benzilate of Potash.}} + 2\ H.$$

Benzilic or *Stilbylic Acid* ($HO, C_{28}H_{11}O_5$) is obtained by decomposing a hot solution of the benzilate of potash, by means of hydrochloric acid: it crystallizes from the solution on cooling, in brilliant needles. Benzilic acid is sparingly soluble in cold water, but is freely dissolved by alcohol and by ether; at 248° it melts to a colourless liquid which becomes red at a higher temperature; when heated still more strongly it is decomposed, emitting fumes of benzoic acid, and violet vapours; the latter may be condensed into a reddish, acrid, oily liquid. Benzilic acid is soluble in oil of vitriol with a beautiful crimson colour, which disappears on diluting the solution. The benzilates are monobasic; those of silver and of lead are white and nearly insoluble.

(1213) *Benzile* ($C_{28}H_{10}O_4$).—When a current of chlorine is transmitted through melted benzoine, so long as hydrochloric acid is evolved, hydrogen is removed and benzile is formed. It may also be obtained more readily by heating benzoine gently with twice its weight of concentrated nitric acid; benzile rises to the surface in the form of a liquid oil which solidifies on cooling; it may be purified by crystallization from ether or from alcohol, and is deposited in beautiful regular six-sided prisms which are of a yellowish colour. Benzile is tasteless, and insoluble in water. It may be fused, and it solidifies again between 194° and 198° into a fibrous mass. At a higher temperature it may be distilled unaltered. Benzile is polymeric with benzoyl, which has not hitherto been isolated. It contains two equivalents less of water than normal benzilic acid. When dissolved in a hot solution of potash it forms a violet-coloured liquid, which by boiling becomes colourless; the benzile assimilating one equivalent of water and becoming converted into benzilate of potash:—

$$\overbrace{C_{28}H_{10}O_4}^{\text{Benzile.}} + KO, HO = \overbrace{KO, C_{28}H_{11}O_5}^{\text{Benzilate of Potash.}}.$$

When benzile is treated with ammonia it gives rise to a series of compounds which contain nitrogen, viz :—

$$1.\quad \overbrace{C_{28}H_{11}NO_2}^{\text{Imabenzile.}} = \overbrace{C_{28}H_{10}O_4}^{\text{Benzile.}} + H_3N - 2\,HO$$

$$2.\quad \overbrace{C_{56}H_{22}N_2O_4}^{\text{Benzilimide.}} = 2(C_{28}H_{10}O_4) + 2\,H_3N - 4\,HO$$

$$3.\quad \overbrace{C_{56}H_{18}N_2}^{\text{Benzilam.}} = 2(C_{28}H_{10}O_4) + 2\,H_3N - 8\,HO.$$

Chloride of Stilbyl, or *of Benzile* ($C_{28}H_{11}O_4$, Cl).—When perchloride of phosphorus is heated with benzilic acid, a violent reaction occurs, chloride of benzile, oxychloride of phosphorus, and hydrochloric acid being formed :—

$$\overbrace{HO,\,C_{28}H_{11}O_5}^{\text{Benzilic Acid.}} + PCl_5 = \overbrace{C_{28}H_{11}O_4,\,Cl}^{\text{Chloride of Stilbyl.}} + HCl + \overbrace{PO_2Cl_3}^{\text{Oxychlor. Phosph.}}.$$

By collecting those portions which distil at a temperature above 482°, chloride of benzile is obtained in the form of a colourless oil which is denser than water. It has a powerful and peculiar odour; it boils at about 518°, and on exposure to air absorbs moisture, and is converted into benzilic and hydrochloric acids; $C_{28}H_{11}O_4,\,Cl + 2HO = HO,\,C_{28}H_{11}O_5 + HCl$.

(1214) Benzoine combines with ammonia, and forms two crystallizable products, which are obtained by digesting benzoine for several weeks in an aqueous solution of ammonia, viz. :—

$$1.\quad \overbrace{C_{84}H_{36}N_4}^{\text{Benzoinamide.}} = \overbrace{3\,(C_{28}H_{12}O_4)}^{\text{Benzoine.}} + 4\,H_3N - 12\,HO\,;$$

$$2.\quad \overbrace{C_{56}H_{24}N_2O_2}^{\text{Benzoinam.}} = 2\,(C_{28}H_{12}O_4) + 2\,H_3N - 6\,HO.$$

Benzoinamide is polymeric with hydrobenzamide; it may be fused when heated, and may be distilled unchanged. It is very sparingly soluble both in alcohol and in ether, even at a boiling temperature.

Besides the compounds already described, there are numerous others derived from the essence of bitter almonds which contain sulphur; but for a description of them the reader is referred to Gerhardt's *Traité de Chimie Organique*, tom. III., and to various memoirs there cited; particularly to one by Laurent (*Ann. de Chimie*, III. i. 291).

(1215) HIPPURIC ACID (HO, $C_{18}H_8NO_5$).—This acid is a constituent of the urine of the herbivora, and is most readily obtained from the urine of the cow, which, according to Boussingault, contains about 1·3 per cent. of it. The urine of the horse also yields hippuric acid if the animal be kept at rest, but if he be kept actively at work the greater part of the hippuric acid disappears, and benzoic acid is found in its stead. Hippuric acid, in minute quantity, is also a normal constituent of human urine, but its amount may be voluntarily increased by taking benzoic acid in any form into the system, since benzoic acid during its passage through the human body becomes converted into the hippuric, and is excreted in this form by the kidneys. If the urine be allowed to become putrid, the hippuric acid is decomposed, and benzoic acid is formed in its place. The facility with which these changes occur is explained by the fact that hippuric acid is truly a colligated benzoic compound. When hippuric acid is boiled for some hours with concentrated hydrochloric acid, it assimilates the elements of water and is resolved into benzoic acid and glycocine, in the following manner:—

$$\overbrace{HO,\ C_{18}H_8NO_5}^{\text{Hippuric Acid.}} + 2\ HO = \overbrace{HO,\ C_{14}H_5O_3}^{\text{Benzoic Acid.}} + \overbrace{HO,\ C_4H_4NO_3}^{\text{Glycocine.}}.$$

Dessaignes has also shown that hippuric acid may be reproduced from chloride of benzoyl and the compound of oxide of zinc with glycocine:—

$$\overbrace{C_{14}H_5O_2Cl}^{\text{Chloride of Benzoyl.}} + \overbrace{ZnO,\ C_4H_4NO_3}^{\text{Oxide of Zinc and Glycocine.}} = ZnCl + \overbrace{HO,\ C_{18}H_8NO_5}^{\text{Hippuric Acid.}}.$$

Preparation.—Hippuric acid may be obtained by adding milk of lime to the fresh urine of cows, boiling for a few minutes, straining from the precipitated phosphates, then adding hydrochloric acid to exact neutralization, and boiling the liquid down to one-eighth of its original bulk; on adding hydrochloric acid in considerable excess to this concentrated liquid, brown crystals of hippuric acid are deposited; they may be dissolved in hot water, and decolorized by transmitting a current of chlorine: the solution on cooling deposits long colourless, transparent needles of hippuric acid. These crystals often become milk-white when kept.

Properties.—Hippuric acid crystallizes in forms derived from the rhombic prism. It requires about 600 times its weight of cold water for solution, and is still less soluble if this liquid be strongly acidulated with hydrochloric acid; boiling water dissolves it readily, so does hot alcohol, but it is nearly insoluble in ether. Hippuric acid has a bitterish taste; its solutions redden litmus powerfully. The acid melts at a gentle heat, and appears to enter into ebullition at about 464°, but it is in reality becoming decomposed; the distillate contains a crystalline sublimate of benzoic acid, and a reddish oil (benzonitrile) which has the agreeable odour of the Tonka bean: hydrocyanic acid is also formed at the same time, and a considerable residue of carbon is left in the retort.

Hippurates.—Hippuric acid is monobasic. Its compounds with the alkalies and with magnesia are very soluble, and are crystallized with difficulty. Acid hippurates of potash and of ammonia may be obtained. *Hippurate of lime* ($CaO, C_{18}H_8NO_5, 3\ Aq$) crystallizes in beautiful rhombic prisms. The *hippurate of lead* is deposited from concentrated solutions in the form of a dense curdy precipitate, but it may be obtained from very dilute boiling solutions in tufts of silky needles with 2 Aq, which gradually become changed into broad brilliant quadrangular plates ($PbO, C_{18}H_8NO_5, 3\ Aq$).

Solutions of the hippurates give white insoluble precipitates with the salts of silver and of mercury: with the persalts of iron they yield a characteristic brown precipitate. The hippurates when in the solid form are readily distinguished by distilling them with hydrate of potash, when they furnish ammonia and benzole.

Hippuric acid is soluble in concentrated nitric acid, and if this solution be mixed with an equal bulk of sulphuric acid, carefully avoiding any elevation of temperature, it produces a *nitro-hippuric* acid ($HO, C_{18}H_7, NO_4, NO_5$), which, when the solution is diluted with three times its bulk of water, is gradually deposited in crystals. If the solution of this acid be boiled with sulphuric or hydrochloric acid it is converted into nitrobenzoic acid and glycocine.

By boiling hippuric acid with a strong solution of potash, it is resolved into a benzoate of the base, and into glycocine. It is also resolved into benzoic acid and glycocine when boiled with concentrated hydrochloric acid, and a similar change occurs if dilute sulphuric, nitric, or oxalic acid be employed instead of the hydrochloric.

Considerable difference of opinion has prevailed respecting the nature of hippuric acid, but the reaction of chloride of benzoyl upon the compound of oxide of zinc with glycocine seems to indicate that this acid is truly *benzoyl-glycocine*, or glycocine in which an equivalent of hydrogen has been displaced by one of benzoyl, the nearly neutral character of glycocine being changed to that of an acid by the addition of the electro-negative radicle benzoyl:—

$$\overbrace{HO,\ C_4H_4NO_3}^{\text{Glycocine.}} \quad ; \quad \overbrace{HO,\ C_4H_3(C_{14}H_5O_2)NO_3}^{\text{Hippuric Acid, or Benzoyl Glycocine.}}.$$

This view is strengthened by the fact that when hippuric acid is boiled with peroxide of lead, carbonic acid is evolved, and benzamide is formed; the oxygen in the peroxide of lead producing the change in the manner illustrated by the following equation:—

$$\overbrace{\mathrm{HO,\ C_4H_3(C_{14}H_5O_2)NO_3}}^{\text{Hippuric Acid.}} + 6\ \mathrm{O} = 2\ \mathrm{HO} + 4\ \mathrm{CO_2} + \overbrace{\mathrm{H_2N,\ C_{14}H_5O_2}}^{\text{Benzamide.}}.$$

(1216) *Benzoglycollic Acid* ($\mathrm{HO,\ C_{18}H_7O_7}$).—Strecker was disposed to regard hippuric acid as an amidated acid; and in order to test this theory he subjected it to the action of nitrous acid, which would liberate the dibasic acid of which it was supposed to be the amidic compound if this view were true. Instead of this he obtained a new monobasic acid, which he termed the *benzoglycollic*, as it is evidently a compound of the benzoic and glycollic acids. Benzoglycollic acid may be obtained by exposing a solution of hippuric acid in nitric acid to the action of a current of binoxide of nitrogen, in which case nitrogen gas is evolved, and benzoglycollic acid is formed. This compound is produced by the reaction of nitrous acid upon hippuric acid, and the action of the binoxide of nitrogen on the nitric acid merely presents nitrous acid in the nascent condition to the hippuric acid; $2\ \mathrm{NO_2} + \mathrm{NO_5} = 3\ \mathrm{NO_3}$. The reaction of nitrous acid upon hippuric acid may be thus represented:—

$$\overbrace{\mathrm{HO,\ C_{18}H_8NO_5}}^{\text{Hippuric Acid.}} + \mathrm{NO_3} = \overbrace{\mathrm{HO,\ C_{18}H_7O_7}}^{\text{Benzoglycollic Acid.}} + \mathrm{HO} + 2\ \mathrm{N}.$$

The binoxide of nitrogen, if not too rapidly transmitted, is wholly absorbed, and when the liquid acquires a green tint the operation may be terminated. Crystals of benzoglycollic acid are deposited as the decomposition proceeds, and on adding water, most of the acid is separated in the crystalline form. It may be purified by converting it into a solution of benzoglycollate of lime, from which the pure acid may be obtained on the addition of hydrochloric acid. Benzoglycollic acid crystallizes in rhomboidal prisms, or in thin plates. It is sparingly soluble in cold water, but is freely dissolved by alcohol and by ether. Boiling water also dissolves, but gradually decomposes it; if the acid be heated with a quantity of water insufficient to dissolve it, it melts to an oily looking liquid; when heated with dilute acids, it is resolved into benzoic and glycollic acids:—

$$\overbrace{2\,(\mathrm{HO,C_{18}H_7O_7})}^{\text{Benzoglycollic Acid.}} + 4\ \mathrm{HO} = \overbrace{2(\mathrm{HO,C_{14}H_5O_3})}^{\text{Benzoic Acid.}} + 2\ \overbrace{\mathrm{HO,C_8H_6O_{10}}}^{\text{Glycollic Acid.}}.$$

The benzoglycollates are monobasic; their solutions may be boiled without undergoing decomposition. Benzoglycollate of soda ($NaO, C_{18}H_7O_7$, 6 Aq) crystallizes readily in large rhomboidal tables. The salt of lime crystallizes in delicate needles which, even when present in small proportion, fill the entire volume of the liquid, and give it a semi-solid appearance. The salts of baryta, zinc and copper, may be readily obtained in crystals; the persalts of iron give a bulky characteristic flesh-coloured precipitate, which is quite insoluble in neutral solutions: the lead salt is insoluble in the cold; but boiling water dissolves it, and on cooling, deposits at first a subsalt, $3\ PbO, 2\ (C_{18}H_7O_7)\ 3\ Aq$, grouped in hemispherical stellate masses; subsequently, thin short needles of the neutral salt crystallize from the solution.

Strecker and Socoloff also obtained a compound of benzoic with lactic acid termed *benzo-lactic acid* ($HO, C_{20}H_9O_7$), by heating the two acids together to about 360°. It is analogous in properties to its homologue benzoglycollic acid.

2. *Essence of Cummin.—Cuminic Series.*

(1217) *Hydride of Cumyl; Essence of Cummin* ($C_{20}H_{11}O_2, H$): *Sp. gr. of vapour* 5·24.—The essential oil obtained by distilling the seeds of the *Cuminum cyminum* with water consists of a mixture of hydride of cumyl and of a hydrocarbon ($C_{20}H_{14}$) termed *cymole*. The hydrocarbon is homologous with benzole (the hydrocarbon obtained by the distillation of dry benzoate of lime), and the oxidized portion is homologous with hydride of benzoyl. Hydride of cumyl is isomeric with essence of aniseed and of fennel.

The two components of the oil of cummin may be readily separated by agitating this oil with a moderately concentrated solution of bisulphite of soda: a crystalline compound is thus formed which yields the pure hydride of cumyl when heated with a solution of potash and submitted to distillation.

Hydride of cumyl boils at 428°, and may be distilled unaltered in vessels from which air is excluded, but if exposed to the air it quickly absorbs oxygen and becomes brown, producing cuminic acid and a resinous compound. Oxidizing agents, such as nitric and chloric acids, also convert the hydride of cumyl into cuminic acid: if it be treated with hydrate of potash, cuminate of potash is produced, whilst hydrogen is liberated.

(1218) *Cuminic acid* ($HO, C_{20}H_{11}O_3$), may be prepared by decomposing cuminate of potash with hydrochloric acid. It crystallizes in colourless plates which emit an odour resembling that of the common bug (*cimex lectularius*). Cuminic acid is fusible, and may be distilled unaltered at about 500°. It is sparingly soluble in water, but freely so in alcohol and in ether. Fuming nitric acid converts it into nitro-cuminic acid. If distilled with an excess of caustic baryta it yields a hydrocarbon ($C_{18}H_{12}$) termed *cumole* which is homologous with benzole. *Cuminic anhydride* may be obtained by decomposing dry cuminate of soda with oxychloride of phosphorus.

The cuminates are monobasic; *cuminate of baryta* ($BaO, C_{20}H_{11}O_3$) forms beautiful iridescent plates: *cuminate of silver* is white, insoluble, and anhydrous; it speedily blackens by exposure to light.

(1219) *Cuminic alcohol* ($C_{20}H_{13}O, HO$; Kraut) may be obtained by treating the essence with an alcoholic solution of potash in the manner directed for preparing benzoic alcohol (1211). It is a colourless oily liquid of an aromatic odour and burning taste: it boils at about 470°, and may be distilled unchanged. It does not absorb oxygen when exposed to the air. When heated with hydrate of potash it yields cymole and cuminic acid. It does not form a colligated acid with sulphuric acid. Cuminic alcohol is isomeric with the oxidized component of oil of thyme.

(1220) *Cumyl* ($C_{20}H_{11}O_2, C_{20}H_{11}O_2$).—When hydride of cumyl is treated with potassium, hydrogen is evolved, and *cumylide of potassium* ($C_{20}H_{11}O_2, K$) is formed, constituting a gelatinous mass, 1 equivalent of which rapidly absorbs 4 equivalents of oxygen from the air, and is converted into cuminate of potash. Water decomposes it into hydrate of potash and hydride of cumyl. When the cumylide of potassium is heated with chloride of cumyl, mutual decomposition occurs, and cumyl is formed:—

$$\overbrace{C_{20}H_{11}O_2, K}^{\text{Cumylide of Potassium.}} + \overbrace{C_{20}H_{11}O_2, Cl}^{\text{Chloride of Cumyl.}} = KCl + \overbrace{C_{20}H_{11}O_2, C_{20}H_{11}O_2}^{\text{Cumylide of Cumyl.}}.$$

Cumyl may be obtained from the result of this reaction by treating the mass first with a weak solution of potash, in order to convert any undecomposed essence of cummin into cuminate of potash; and then agitating it with ether; the supernatant ethereal layer which contains the cumyl in solution is dried over chloride of calcium, and heated gently to expel the ether, when pure cumyl is left. Cumyl presents the appearance of a viscous oil which is heavier than water; when gently heated it emits an agreeable odour like that of the geranium. It is freely soluble in boiling alcohol, and cannot be distilled without undergoing decomposition;

hydrate of potash converts it into cuminate of potash, whilst a portion of oil of cummin is simultaneously produced :—

$$\overbrace{C_{20}H_{11}O_2, C_{20}H_{11}O_2}^{\text{Cumyl.}} + KO, HO = \overbrace{C_{20}H_{11}O_2, H}^{\text{Hydride of Cumyl.}} + \overbrace{KO, C_{20}H_{11}O_3}^{\text{Cuminate of Patash.}}.$$

(1221) *Chloride of Cumyl* or *Cuminic oxychloride* ($C_{20}H_{11}O_2$, Cl); *Sp. gr.* 1·070.—This is a colourless mobile liquid which boils at about 495°. It is obtained by distilling cuminic acid with perchloride of phosphorus.

Many other compounds of the cuminic series may be formed, analogous to those of the benzoic series which have been already described.

The homologous oils, $C_{16}H_7O_2$, H, and $C_{18}H_9O_2$, H, intermediate between hydride of benzoyl and hydride of cumyl have not as yet been discovered, but the acid corresponding to the first of these, the *toluic* (or toluylic), is known. It may be procured by oxidizing cymole by long-continued boiling with nitric acid which has been diluted with about six times its bulk of water; and it is probable that by Piria's process of treating the lime salt of this acid with formiate of lime (*note*, p. 462), the aldehyd (or the missing hydride), $C_{16}H_7O_2$, H, would be obtained.

3. *Essence of Cinnamon.—Cinnamic Series.*

(1222) *Oil of Cinnamon: Hydride of Cinnamyl* ($C_{18}H_7O_2$, H).—Essence of cinnamon and essence of cassia consist chiefly of hydride of cinnamyl, with a small proportion of a hydrocarbon isomeric with oil of turpentine. The commercial essence has a sp. gr. varying between 1·025 and 1·05. It boils at from 430° to 445°. Hydride of cinnamyl is readily obtained in a state of purity by agitating the crude essence with a solution of bisulphite of potash. The crystalline product thus obtained must be pressed, washed with cold alcohol, and dried; after which it must be dissolved at a gentle heat in dilute sulphuric acid: the hydride of cinnamyl then collects upon the surface of the liquid in the form of a colourless fragrant oil. This oil is slightly heavier than water; it rapidly absorbs oxygen from the air and becomes yellow, owing to the formation of a solid resin, mixed with cinnamic acid. Nitric acid combines with the hydride and converts it into a solid mass of crystals. This compound is immediately decomposed by water into nitric acid and free hydride of cinnamyl. Dumas made use of this fact in separating the hydride from its associated hydrocarbon.

If hydride of cinnamyl be boiled with nitric acid, abundance of hydride of benzoyl is evolved, and benzoic acid is found in the solution. If the essence be boiled with chloride of lime, benzoate of lime is produced. Chiozza has also made the interesting observation that hydride of benzoyl may be converted into oil of cinnamon by dissolving the pure hydride of benzoyl in aldehyd, and saturating the mixture with hydrochloric acid gas: on the application of a gentle heat the liquid becomes brown; and on afterwards proceeding to distillation, oil of bitter almonds first passes over, and then oil of cinnamon. Oil of cinnamon may, in fact, be regarded as hydride of benzoyl in which an equivalent of hydrogen has been displaced by an equivalent of acetyl (C_4H_3), in which case the reaction in the foregoing experiment might be thus represented; water being eliminated under the influence of the hydrochloric acid, which is not indicated in the equation:—

$$\overbrace{C_{14}H_5O_2, H}^{\text{Hydride of Benzoyl.}} + \overbrace{C_4H_3O_2, H}^{\text{Aldehyd.}} = \overbrace{C_{14}H_4(C_4H_3)O_2, H}^{\text{Hydride of Cinnamyl.}} + 2\,HO.$$

With ammonia the oil of cinnamon forms a crystalline solid termed *cinnhydramide*, which is analogous to hydrobenzamide:—

$$3\,\overbrace{(C_{18}H_7O_2, H)}^{\text{Hydride of Cinnamyl.}} + 2\,H_3N = \overbrace{C_{54}H_{24}N_2}^{\text{Cinnhydramide.}} + 6\,HO.$$

Several chlorinated substitution compounds may be obtained from oil of cinnamon: one of these, *chlorocinnose* ($C_{18}H_3Cl_4O_2$, H), crystallizes in white needles, which are fusible and may be volatilized without decomposition.

(1223) *Cinnamic Acid* (HO, $C_{18}H_7O_3$).—When hydride of cinnamyl is heated with hydrate of potash, hydrogen is evolved, and cinnamate of potash is formed:—

$$\overbrace{C_{18}H_8O_2}^{\text{Hydride of Cinnamyl.}} + KO, HO = \overbrace{KO, C_{18}H_7O_3}^{\text{Cinnamate of Potash.}} + 2\,H.$$

This acid is contained in many balsams, such as those of storax, of tolu, and of Peru; and it is sometimes deposited in old specimens of essence of cinnamon. It may be extracted from storax and from balsam of tolu after distilling off the portion which can be volatilized by distillation with water, by treating the residue with weak solutions of carbonate of soda; the acid may be precipitated from the impure cinnamate of soda by the addition of hydrochloric acid.

Pure cinnamic acid is soluble in boiling water, from which it crystallizes in brilliant plates. Alcohol dissolves it with facility. It fuses at 264°, and at 560° it enters into ebullition, and may be distilled unaltered.

Nitric acid converts it into *nitro-cinnamic* acid ($HO, C_{18}H_6, NO_4, O_3$) if care be taken to avoid heating the mass; otherwise it is decomposed, and hydride of benzoyl is formed, which is converted, by continuing the action, into benzoic and nitro-benzoic acids. If cinnamic acid be distilled with bichromate of potash and sulphuric acid it yields hydride of benzoyl. When fused with an excess of hydrate of potash it is resolved into acetic and benzoic acids, whilst hydrogen is liberated:—

$$\overbrace{HO, C_{18}H_7O_3}^{\text{Cinnamic Acid.}} + 2\,(KO, HO) = \overbrace{KO, C_4H_3O_3}^{\text{Acetate of Potash.}} + \overbrace{KO, C_{14}H_5O_3}^{\text{Benzoate of Potash.}} + 2\,H.$$

These reactions clearly indicate a close relation between cinnamic and benzoic acids. Indeed, cinnamic acid may be regarded as benzoic acid in which one equivalent of hydrogen has been displaced by acetyl (C_4H_3); thus $HO, C_{18}H_7O_3 = HO, C_{14}H_4(C_4H_3)\,O_3$.

The cinnamates are monobasic salts; those of the alkalies are readily soluble and are crystallizable. A solution of these salts gives a yellow precipitate with the persalts of iron.

If cinnamic acid be intimately mixed with four times its weight of caustic baryta and distilled, it loses carbonic acid, and becomes converted into cinnamole, a hydrocarbon which bears the same relation to the cinnamic series that benzole does to the benzoic:—

$$\overbrace{HO, C_{18}H_7O_3}^{\text{Cinnamic Acid.}} + 2\,BaO = \overbrace{C_{16}H_8}^{\text{Cinnamole.}} + 2\,(BaO, CO_2).$$

When cinnamic acid is distilled with perchloride of phosphorus it yields a compound corresponding to chloride of benzoyl. It may be termed *chloride of cinnamyl*, or *cinnamic oxychloride* ($C_{18}H_7O_2, Cl$).

(1224) *Styrone; Peruvine; Cinnamic Alcohol* ($HO, C_{18}H_9O$).—This substance is procured by the distillation of styracin, or metacinnamene ($C_{36}H_{16}O_4$; 1226) with a concentrated solution of potash or of soda: a milky liquid passes over, from which on saturating it with common salt a whitish cream rises to the surface, and gradually solidifies. According to Toel, cinnamic alcohols may be obtained in beautiful silky needles, which have an agreeable odour of hyacinths: it fuses at 91°, and may be distilled unaltered. Nitric acid liberates hydride of benzoyl from it.

No ethers corresponding to this supposed alcohol have as yet been obtained. When exposed to the action of atmospheric air under the influence of platinum black it yields oil of cinnamon, the aldehyd of this alcohol (Strecker).

(1225) The *Storax* from which the preceding compound is obtained is a gum-resin of the consistence of honey, and of a brownish-grey colour; it has a powerful oppressive odour and an aromatic taste, and consists of a mixture of styracin, of cinnamic acid, of a peculiar resin, and of styrole, which is an essential oil isomeric with cinnamole.

Styrole ($C_{16}H_8$, *Sp. gr. of liquid* 0·924) is distinguished from cinnamole by the remarkable change which it experiences on the application of a temperature of about 400°, when it becomes converted into a polymeric solid termed *metastyrole*, or *draconyl*. In order to obtain styrole, three parts of storax, and one of carbonate of soda, should be subjected to distillation with water: the alkali retains the cinnamic acid, and the styrole passes over. It may be distilled at 294°; but during this operation the residue in the retort is apt suddenly to rise in temperature, and to be converted into metastyrole. Styrole also comes over mixed with toluole, when the resin termed dragon's-blood (from the *Dracæna draco*) is submitted to distillation. Styrole is a very mobile, colourless oil, endowed with an aromatic persistent odour, recalling that both of benzole and of naphthalin. When treated with bichromate of potash and dilute sulphuric acid styrole is converted into benzoic acid.

Metastyrole is polymeric with styrole and with cinnamole; it is a colourless solid of high refracting power, and is destitute both of smell and taste. It softens on the application of heat, and may be drawn out into threads. It is insoluble in water and in alcohol, and is but very sparingly soluble in ether. When subjected to a high temperature it may be distilled, and is re-converted into styrole; and this liquid may be again reduced to the solid form of metastyrole by heating it to 400° in a sealed tube.

(1226) Two other balsams, closely resembling storax, are also met with as articles of commerce, viz., the balsams of Peru and of tolu.

Balsam of Peru is a fragrant resin produced by several species of leguminous plants of the genus *Myrospermum*. It is sold in the form either of a hard resin, or of a black, semi-solid body, which contains a peculiar resin and two other closely related substances, viz. *cinnamic acid*, and *metacinnamene*, or *styracin*.

Styracin ($C_{36}H_{16}O_4$) is a crystallizable solid, which is freely soluble in alcohol and in ether; it is polymeric with hydride of cinnamyl: it fuses at 111°. When treated with potash it undergoes a change analogous to saponification, and furnishes cinnamic acid and styrone :—

$$\overbrace{C_{36}H_{16}O_4}^{\text{Styracin.}} + KO, HO = \overbrace{KO, C_{18}H_7O_3}^{\text{Cinnam. Potash.}} + \overbrace{C_{18}H_{10}O_2}^{\text{Styrone.}}.$$

Balsam of Tolu is stated to be the produce of the *Myrospermum toluiferum*. It is met with in commerce, in the form either of a rusty brown, semi-transparent resin, or in that of a soft, dark coloured, transparent balsam, of the consistence of turpentine, with a remarkably fragrant and agreeable odour. It is composed of the same substances as the balsam of Peru, but the proportion of styracin is much smaller. The solid resinous portion, according to E. Kopp, consists of two resins which have the composition of hydrated oxides of styracin: styracin being $C_{36}H_{16}O_4$; resin α being 2 HO, $C_{36}H_{16}O_6$; and resin β, 4 HO, $C_{36}H_{16}O_6$. When balsam of tolu is distilled, it yields benzoic ether and a hydrocarbon ($C_{14}H_8$) termed toluole.

4. *Oil of Spiræa—Salicylic Series.*

(1227) *Hydride of Salicyl; Salicylous Acid* (H, $C_{14}H_5O_4$) : *Sp. gr. of liquid* 1·173; *of vapour* 4·276.—When the flowers of the meadow-sweet (*Spiræa ulmaria*) are distilled with water they yield an essential oil which consists chiefly of a fragrant compound termed *hydride of salicyl*, but which also contains a small quantity of a hydrocarbon isomeric with oil of turpentine, and a crystalline substance analogous to camphor. If the essence be agitated with a solution of potash, the hydride of salicyl is dissolved, and can afterwards be separated by the addition of an acid. It is, however, generally obtained by the decomposition of salicin (1234) by means of bichromate of potash: 2 parts of salicin and 2 of bichromate of potash are to be mixed with 16 parts of water in a retort, and 3 parts of oil of vitriol diluted with 8 of water are to be added; a slight reaction commences, attended with extrication of heat, and a sparing disengagement of gas: as soon as this has ceased a gentle heat may be applied, and oil of spiræa passes over and collects in the receiver in the form of a heavy oil. Carbonic and formic acids are produced at the same time, whilst chrome alum remains in the retort. 25 parts of salicin yield about 6 of the essence.*

Hydride of salicyl is a colourless oil, which by exposure to the air speedily assumes a more or less intense red tint. It boils is 396° (Ettling), and becomes solid at —4°. Hydride of salicyl possesses the properties of an acid; it decomposes the carbonates with effervescence, and yields crystallizable salts. It forms with potash and soda both neutral and acid salts, which are permanent when dry, but when moist they undergo spontaneous decomposition, and become black. The neutral potash salt ($K, C_{14}H_5O_4, 2\ Aq$) is soluble in alcohol. The acid salt ($K, C_{14}H_5O_4 + H, C_{14}H_5O_4$) is sparingly soluble in water, but crystallizes from boiling alcohol in groups of delicate needles. A solution of salicylide of potassium gives yellow insoluble precipitates with the salts of baryta, manganese, lead, silver, and with the salts of both the oxides of mercury; salicylide of copper is of a green colour, but the most characteristic reaction of hydride of salicyl is the production of an intense violet colour with the persalts of iron, which gradually disappears by exposure to the air.

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* Büchner states that the unexpanded flower buds of the meadow-sweet contain salicin, and this substance, during flowering, by exposure to the air, absorbs oxygen, and thus furnishes hydride of salicyl.

Ammonia transforms hydride of salicyl into *salhydramide*, $C_{42}H_{18}N_2O_6$ (1049).

(1228) *Hydride of Chloro-salicyl*, or *Chlorosalicylous Acid* ($H, C_{14}H_4ClO_4$).—This substance was formerly termed chloride of salicyl,* but its reactions show that it is more correctly regarded as salicylous acid in which an equivalent of hydrogen has been displaced by chlorine. It is procured by transmitting a current of dry chlorine gas through oil of spiræa, gently heated: copious evolution of hydrochloric acid ensues, and as soon as this ceases to be evolved the transformation is complete; on allowing the mass to cool, the compound crystallizes. It may be dissolved in boiling alcohol, which deposits it on cooling in colourless, rectangular, glistening plates. It melts at a gentle heat, and may be sublimed without decomposition. This substance is insoluble in water, but soluble in ether and in oil of vitriol. The alkalies dissolve it and form crystallizable salts. The chloro-salicylide of barium ($Ba, C_{14}H_4ClO_4, Aq$) forms a yellow, crystalline, sparingly soluble powder.

Corresponding compounds may be obtained, which contain respectively an equivalent of bromine and an equivalent of peroxide of nitrogen, in the place of the equivalent of chlorine. These bodies likewise combine with the alkalies and form crystallizable salts.

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* Gerhardt has obtained a compound which appears to be the true *chloride of salicyl* ($C_{14}H_5O_4, Cl$) by the action of perchloride of phosphorus on oil of winter-green. It is a fuming, slightly coloured liquid, which evolves heat when mixed with water, whilst the chloride is converted into salicylic and hydrochloric acids; $C_{14}H_5O_4, Cl + 2\ HO = HO, C_{14}H_5O_5 + HCl$.

(1229) It will be observed that hydride of salicyl is metameric with benzoic acid. It is, however, supposed to be formed by the union of hydrogen with a peculiar radicle, termed *salicyl* ($C_{14}H_5O_4$), which contains 2 equivalents more of oxygen than benzoyl. Although neither salicyl nor benzoyl has been isolated, yet a compound of the two, *salicylide of benzoyl* ($C_{14}H_5O_2$, $C_{14}H_5O_4$) is known; this substance may be procured by the action of chloride of benzoyl on hydride of salicyl (Cahours):—

$$\left.\begin{matrix}\overbrace{C_{14}H_5O_4}^{\text{Hydr. Salicyl.}}\\ H\end{matrix}\right\} + \left.\begin{matrix}\overbrace{C_{14}H_5O_2}^{\text{Chlor. Benzoyl.}}\\ Cl\end{matrix}\right\} = \left.\begin{matrix}\overbrace{C_{14}H_5O_4}^{\text{Salicyl. Benzoyl.}}\\ C_{14}H_5O_2\end{matrix}\right\} + \left.\begin{matrix}H\\ Cl\end{matrix}\right\}.$$

It is a yellow crystalline solid which fuses at 260°, and may be sublimed at about 356°. It is identical with the *parasalicyl* of Ettling, obtained by the distillation of salicylide of copper.

If hydride of salicyl be fused with hydrate of potash, hydrogen is liberated, and a new acid is formed, which stands in the same relation to hydride of salicyl that benzoic acid does to hydride of benzoyl; thus:—

$$\overbrace{H,\ C_{14}H_5O_4}^{\text{Hydride of Salicyl.}} + KO,\ HO = \overbrace{KO,\ C_{14}H_5O_5}^{\text{Salicylate of Potash.}} + 2\ H.$$

The following table gives a synoptic view of the principal compounds related to the oil of spiræa, embracing the compounds of the salicyl series:—

Hydride of salicyl (Salicylous acid) .	$H,C_{14}H_5O_4$
Salicylide of potassium	$K,C_{14}H_5O_4$, 2 Aq
Acid do. do.	$K,C_{14}H_5O_4 + H,C_{14}H_5O_4$
Hydride of chlorosalicyl . . .	$H,C_{14}H_4ClO_4$
Chlorosalicylide of barium . . .	$Ba,C_{14}H_4ClO_4$, Aq
Hydride of bromosalicyl . . .	$H,C_{14}H_4BrO_4$
Hydride of nitrosalicyl . . .	$H,C_{14}H_4,NO_4,O_4$
Chloride of salicyl	$Cl,C_{14}H_5O_4$
Salicylide of benzoyl (Parasalicyl) . .	$C_{14}H_5O_2,C_{14}H_5O_4$
Salicylic anhydride	$C_{14}H_5O_5,C_{14}H_5O_5$
Salicylide	$C_{28}H_8O_8$
Salicylic acid . . .	$HO,C_{14}H_5O_5$
Salicylate of potash	$KO,C_{14}H_5O_5$, Aq
Salicylate of copper and potash . .	$KO,C_{14}H_4CuO_5$, 2 Aq
Nitrosalicylic . . **(Anilic) acid** . .	$HO,C_{14}H_4,NO_4,O_5$
Dinitrosalicylic do.	$HO,C_{14}H_3(NO_4)_2O_5$
Chlorosalicylic do.	$HO,C_{14}H_4ClO_5$
Dichlorosalicylic do.	$HO,C_{14}H_3Cl_2O_5$

Oil of winter-green (Salicylate of methyl or Gaultheric acid)	$C_2H_3O,C_{14}H_5O_5$ or $HO,C_{14}H_4(C_2H_3)O_6$
Gaultherate of potash	$KO,C_{14}H_4(C_2H_3)O_6$
Gaultherate of methyl	C_2HO_3, $C_{14}H_4(C_2H_3)O_6$
Salhydramide . .	$C_{42}H_{18}N_2O_6$
Thiosalicole . .	$C_{14}H_6O_2S_2$
Salicin	$C_{26}H_{18}O_{14}$
Chlorosalicin . .	$C_{26}H_{17}ClO_{14}$, 4 Aq
Dichlorosalicin .	$C_{26}H_{16}Cl_2O_{14}$, 2 Aq
Trichlorosalicin .	$C_{26}H_{15}Cl_3O_{14}$, 2 Aq
Helicin	$2\,(C_{26}H_{16}O_{14})$ 3 Aq
Helicoidin .	$C_{26}H_{18}O_{14}$, $C_{26}H_{16}O_{14}$, 3Aq
Saligenin . . .	$C_{14}H_8O_4$
Chlorosaligenin .	$C_{14}H_7ClO_4$
Dichlorosaligenin	$C_{14}H_6Cl_2O_4$
Trichlorosaligenin	$C_{14}H_5Cl_3O_4$
Saliretin . . .	$C_{14}H_6O_2$
Populin or Benzoyl-salicin .	$C_{40}H_{22}O_{16}$, 4 Aq; or $C_{26}H_{17}(C_{14}H_5O_2)O_{14}$, 4 Aq
Benzoyl-helicin . .	$C_{26}H_{15}(C_{14}H_5O_2)O_{14}$
Coumarin . . .	$C_{18}H_6O_4$

(1230) *Salicylic Acid* ($HO, C_{14}H_5O_5$).—This compound may be obtained also by fusing hydrate of potash in a silver capsule, and adding salicin in small quantities at a time, taking care not to allow the temperature to rise beyond 750°. On adding hydrochloric acid to the mass after it has been dissolved in water, salicylic acid is precipitated. The acid is also readily prepared from the oil of winter-green, by boiling it for a few minutes with a solution of caustic potash; in this operation wood spirit is liberated, and on the addition of an acid, salicylic acid is precipitated. Coumarin (1236) also yields this acid when exposed to similar treatment. It is likewise obtained by decomposing anthranilic acid (1287) with nitrous acid.

Salicylic acid is sparingly soluble in cold water, but is readily dissolved by boiling water, from which it crystallizes on cooling in long slender needles. It fuses at 316°, and if pure, may at a higher temperature be sublimed unaltered. When salicylic acid is distilled with an excess of lime, it yields carbonic and phenic (carbolic) acids :—

$$\overbrace{HO, C_{14}H_5O_5}^{\text{Salicylic Acid.}}, \quad + \quad 2\,CaO \quad = \quad 2\,(CaO, CO_2) \quad + \quad \overbrace{HO, C_{12}H_5O}^{\text{Phenic Acid.}}.$$

The monobasic salicylates of the alkalies yield pure phenic acid on distillation.

Salicylates.—Salicylic acid forms compounds which are in many respects anomalous. It is generally considered to be a monobasic acid, but it forms two distinct classes of salts, one of which contains one equivalent, the other two equivalents of base; the acid, therefore, has been represented by the formula $HO, C_{14}H_5O_5$, as well as by that of $2\,HO, C_{14}H_4O_4$. The monobasic salts may be preserved unaltered in a dry state, but they become brown if exposed to the air in a moist condition.

The soluble salicylates are characterized by the property which they possess, of forming an inky blue precipitate when mixed with solutions of the persalts of iron. This colour disappears on the addition of free hydrochloric acid. The anomalous character of the salicylates renders their constitution an object of considerable interest, and we shall therefore describe a few of these compounds.

The *monobasic salicylate of potash* ($KO, C_{14}H_5O_5$, Aq) crystallizes from its alcoholic solution in silky needles. Piria, (Liebig's *Annal.* xciii., 262), has obtained a double *salicylate of copper and potash* ($KO, C_{14}\left.\begin{matrix}H_4\\Cu\end{matrix}\right\}O_5$, 4 Aq), which crystallizes in large emerald green plates. The ordinary *lime* salt ($CaO, C_{14}H_5O_5$, 2 Aq) is very soluble, and crystallizes in octohedra of great beauty. If a solution of this salt be mixed with a solution of lime in syrup, a *dibasic salicylate of lime* ($CaO, C_{14}\left.\begin{matrix}H_4\\Ca\end{matrix}\right\}O_5$, 2 HO), which is sparingly soluble in water, is deposited in hard crystalline grains. The aqueous solution of this salt has an alkaline reaction, and is decomposed by the action of carbonic acid, carbonate of lime being formed, and the monobasic lime salt being set free. A similar salt may be obtained with *baryta* ($BaO, C_{14}\left.\begin{matrix}H_4\\Ba\end{matrix}\right\}O_5$, 4 Aq); if heated to 212° it loses 4 equivalents of water. With lead, salicylic acid forms three distinct compounds: the *monobasic salicylate of lead* ($PbO, C_{14}H_5O_5$, Aq) is a sparingly soluble salt, which is crystalline and has a silky lustre. If tribasic acetate of lead be added to a boiling solution of this salt, a *dibasic salicylate of lead* is deposited as a heavy, white, crystalline, anhydrous powder ($PbO, C_{14}\left.\begin{matrix}H_4\\Pb\end{matrix}\right\}O_5$; but if the solution be decomposed by adding an excess of ammonia, instead of the tribasic acetate of lead, the liquid when boiled deposits a *pentabasic lead salt* ($4\ PbO, C_{14}\left.\begin{matrix}H_4\\Pb\end{matrix}\right\}O_5$).

These anomalies may be explained by supposing that the normal salts of salicylic acid are monobasic, but that a second equivalent of hydrogen in the radicle of the acid admits of being displaced by a metal, thus giving rise to a series of salts which present the characters of basic salts.

Gerhardt has found (*Ann. de Chimie*, III. xlv. 90) that this second equivalent of hydrogen in the radicle is displaceable by benzoyl, and other electro-negative groups. The mode of forming these compounds will be best understood after the properties of the salicylate of methyl, or oil of wintergreen, have been described.

(1231) *Salicylate of Methyl; Oil of Winter-green,* or *Gaultheric Acid* ($C_2H_3O, C_{14}H_5O_5 = HO, C_{14}H_4\ (C_2H_3)\ O_5$); *Sp. gr. of liquid* 1·18; *of vapour* 5·42.—The flowers of the *Gaultheria procumbens* furnish an essence consisting chiefly of salicylate of methyl, mixed with a small proportion of a hydrocarbon, termed *gaultherilene,* which is isomeric with oil of turpentine. This hydrocarbon boils at 320°, and constitutes the more volatile portion of the essence; the salicylate of methyl is procured by collecting separately those portions which come over after the boiling point has risen to 432°, at which point it continues stationary. It may also be obtained artificially by distilling a mixture of 2 parts of crystallized salicylic acid, 2 of anhydrous wood spirit, and 1 part of oil of vitriol.

In whichever mode it is obtained it presents the appearance of a colourless or yellowish oil, of a powerful, agreeable, and persistent odour. It is sparingly soluble in water, and its aqueous solution acquires a violet tint when mixed with a persalt of iron. Several substitution products, containing chlorine, bromine, and peroxide of nitrogen, may be obtained from the essence.

Salicylate of methyl is metameric with anisic acid; it possesses feeble acid properties, and if mingled with a cold concentrated solution of potash it becomes converted into a crystalline mass, termed *gaultherate* of potash ($KO, C_{14}H_4 (C_2H_3) O_5$), which may be obtained in a state of purity by recrystallization from alcohol. This salt is completely soluble in water; on the addition of an acid to the aqueous solution the salicylate of methyl is separated unaltered, but if the solution be heated with an excess of alkali, wood spirit is liberated, and a salicylate of potash is formed. The essence of gaultheria may be regarded as existing in this compound in the form of salicylic acid, in which an equivalent of hydrogen has been displaced by an equivalent of methyl. If the solution of gaultherate of potash be mixed with salts of baryta, of lead, or of mercury, insoluble gaultherates of these bases are precipitated.

(1232) *Other Ethers of Salicylic Acid.*—The other ethers of salicylic acid also present the properties of acids, and Cahours has made the singular discovery that they may be again etherified; thus a gaultherate of methyl ($C_2H_3O, C_{14}H_4 (C_2H_3) O_5$) may be procured, which it will be observed corresponds exactly with the dibasic salts of salicylic acid; the dibasic lead salt, for instance, being ($PbO, C_{14}H_4 (Pb) O_5$). The salicylic ethers may be acted upon by chlorine, so as to yield substitution compounds, but the action of chlorine upon these ethers is anomalous. In the case of the compound ethers generally, the ethylic, or methylic portion is that which is first attacked, but in the salicylic ethers, it is the acid constituent which first experiences the displacement of its hydrogen, so that the first step in the reaction is the formation of a chlorosalicylic ether.

Induced by considerations arising partially out of these facts, Gerhardt was led to attempt the formation of ethers in which the salicylates of methyl and of ethyl should act the part of an alcohol; and he succeeded in obtaining compounds corresponding to the ethers:—thus, if chloride of benzoyl (benzoic oxychloride) be made to act upon oil of gaultheria, a compound is obtained, termed *benzoate of methyl-salicyl* ($C_{14}H_4, C_2H_3, O_5, C_{14}H_5O_3$), which crystallizes in rhombic prisms :—

$$\overbrace{\left.\begin{matrix}C_{14}H_4(C_2H_3)O_4\\H\end{matrix}\right\}O_2}^{\text{Salicylate of Methyl.}} + \overbrace{\left.\begin{matrix}C_{14}H_5O_2\\Cl\end{matrix}\right\}}^{\text{Chlor. Benzoyl.}} = \overbrace{\left.\begin{matrix}C_{14}H_4(C_2H_3)O_4\\(C_{14}H_5O_2)\end{matrix}\right\}O_2}^{\text{Benzoate of Methyl-salicyl.}} + \begin{matrix}H\\Cl\end{matrix};$$

and by employing an oxychloride of a dibasic acid, such as the succinic, a dibasic ether, *succinate of methyl-salicyl* [2 ($C_{14}H_4$, C_2H_3, O_5), $C_8H_4O_6$] may be formed, and obtained crystallized from its alcoholic solution in fibrous rectangular plates.

(1233) *Salicylic anhydride* ($C_{14}H_5O_5$, $C_{14}H_5O_5$) may be procured by the action of oxychloride of phosphorus on dry salicylate of soda; at the same time a quantity of *salicylide* ($C_{28}H_8O_8$) is produced. The latter body is analogous to lactide (1104); it contains two equivalents of water less than are present in salicylic anhydride. Both salicylide and salicylic anhydride are rapidly converted into ordinary salicylic acid, when heated with a solution of potash.

When salicylic acid is swallowed, a portion of it finds its way into the urine, but it becomes converted into a crystallizable colligated combination of glycocine, termed *salicyluric acid* ($HO, C_{14}H_8NO_7$) by a process analogous to that which converts benzoic acid, under similar circumstances, into hippuric acid. The solutions of salicyluric acid give a violet colour with persalts of iron. When boiled with concentrated hydrochloric acid, salicyluric acid splits up into salicylic acid and glycocine.

Portions of the hydrogen in salicylic acid may be displaced by chlorine and by bromine, forming *chlorosalicylic* and *dichlorosalicylic, bromosalicylic* and *dibromosalicylic* acids. A mixture of hydrochloric acid and chlorate of potash converts salicylic acid into chloranile (perchlorokinone) $C_{12}Cl_4O_4$.

Fuming nitric acid converts the salicylic into *nitro-salicylic* (indigotic or anilic) acid, ($HO, C_{14}H_4, NO_4, O_5$), and by prolonged digestion with it furnishes carbazotic acid ($HO, C_{12}H_2(NO_4)_3O$). Nitrosalicylic acid may also be obtained by adding indigo in small quantities at a time to boiling nitric acid, which has been previously diluted with ten or twelve parts of water: as the liquid cools the acid crystallizes. It is sparingly soluble in cold water, but freely so in boiling water and in alcohol: it fuses easily, and may be sublimed unaltered at a gentle heat. Its solutions when mixed with the persalts of iron give a red colour. With salts of lead it gives a pale yellow voluminous precipitate (PbO, $C_{14}H_4NO_4$, O_5, Aq). The salts of potash and of ammonia may be obtained in orange-coloured silky needles. A *dinitrosalicylic acid* [$HO, C_{14}H_3(NO_4)_2O_5$] may also be formed.

(1234) Salicin ($C_{26}H_{18}O_{14}$).—This substance has been made the subject of a series of interesting researches by Piria (*Ann. de Chimie*, II. lxix. 281, and III. xiv. 257). Salicin is contained in the bark of most of the willows, and confers upon them their peculiar bitterness. It is procured by adding to an aqueous infusion of the bark, hydrated oxide of lead, by which the tannin and colouring matters are removed, and then on filtering and evaporating the liquid the salicin is obtained in crystals. It is soluble in five or six parts of cold water, and is still more readily dissolved by alcohol. These solutions exert a left-handed rotatory action upon a ray of polarized light. A solution of salicin is not precipitated by infusion of gelatin, nor by one of tannin, but with an ammoniacal solution of acetate of lead it yields a precipitate consisting of $C_{26}H_{14}Pb_4O_{14}$. When salicin is moistened with strong sulphuric acid it acquires a deep red colour, and a compound acid is formed which has been termed *sulpho-rufic* acid.

When salicin is boiled for a few minutes with dilute sulphuric or hydrochloric acid a remarkable change occurs; grape sugar is found in the solution, and, on neutralizing the acid, the liquid strikes a very intense blue with the persalts of iron, owing to the presence of *saligenin* ($C_{14}H_8O_4$). On agitating the solution with ether, the saligenin is separated, and may be obtained on evaporation crystallized in pearly tables, which fuse at 180°. A similar transformation is effected when salicin is mixed with a solution of synaptase (*note* p. 407). The change which occurs may be thus represented:—

$$\overbrace{C_{26}H_{18}O_{14}}^{\text{Salicin.}} + 4\,HO = \overbrace{C_{14}H_8O_4}^{\text{Saligenin.}} + \overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}.$$

By heating saligenin carefully in close vessels two equivalents of water are expelled, and a resinous body named *saliretin* ($C_{14}H_6O_2$) remains. The same effect is produced by boiling salicin or saligenin for some time with a dilute acid; the solution becomes turbid and deposits the resin, which is insoluble in water, but soluble in alcohol, ether, and concentrated acetic acid. It acquires a red colour when moistened with oil of vitriol.

When salicin is heated to 248° it fuses, and at a higher temperature is completely decomposed. If heated with hydrate of potash it is also decomposed, and oxalate and salicylate of potash are formed. Concentrated nitric acid converts salicin into oxalic and carbazotic acids. If salicin be boiled with sulphuric acid and peroxide of manganese, formic acid is the principal product. But the most interesting transformation of which it is susceptible is that produced by chromic acid:—if 1 part of salicin be mixed with 1 part of bichromate of potash, 1½ of sulphuric acid, and 20 parts of water, on the application of a gentle heat formic and carbonic acids are produced, whilst a fragrant oily liquid distils over with the vapour of water, and condenses in the receiver; it has exactly the odour of the meadow-sweet or the heliotrope, and analysis has proved it to have the same composition ($C_{14}H_6O_4$) as the essential oil of these plants. Both saligenin and saliretin also yield oil of spiræa when treated with bichromate of potash and sulphuric acid, the change effected being simply one of oxidation:—

$$\overbrace{C_{14}H_8O_4}^{\text{Saligenin.}} + O_2 = \overbrace{H,\ C_{14}H_5O_4}^{\text{Oil of Spiræa.}} + 2\ HO;\ \text{and}$$

$$\overbrace{C_{14}H_6O_2}^{\text{Saliretin.}} + O_2 = \overbrace{H,\ C_{14}H_5O_4}.$$

Chlorine produces three different substitution products with salicin; viz., $C_{26}H_{17}ClO_{14}$; $C_{26}H_{16}Cl_2O_{14}$; and $C_{26}H_{15}Cl_3O_{14}$. When digested with emulsin they each furnish a corresponding chlorinated form of saligenin (see table, p. 481), and if boiled with dilute acids each yields a corresponding chlorinated form of saliretin.

Helicin 2 ($C_{26}H_{16}O_{14}$), 3 Aq.—When one part of salicin is digested without the application of heat in 10 parts of nitric acid of sp. gr. 1·160 for twenty-four hours, it becomes gradually dissolved, and loses 2 equivalents of hydrogen; the solution acquires a yellow colour, and crystals of helicin are deposited: the mother liquor must be removed by submitting the crystals to pressure in linen, after which they must be washed with cold water and with ether, which leaves them in a state of purity. Helicin crystallizes in small delicate colourless needles, which are very soluble in boiling water and in alcohol, but not in ether. It has a bitterish taste; when heated to 212° it loses its water of crystallization; it fuses at 347°, and is gradually decomposed, becoming converted into an insoluble resinoid mass. Under the influence of alkalies, or of emulsin, helicin assimilates the elements of water and is converted into oil of spiræa, and glucose:—

$$\overbrace{C_{26}H_{16}O_{14}}^{\text{Helicin.}} + 4\ HO = \overbrace{C_{14}H_6O_4}^{\text{Oil of Spiræa.}} + \overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}.$$

Dilute nitric acid also decomposes helicin, and liberates oil of spiræa. When boiled with dilute nitric acid, nitrosalicylic ($HO,\ C_{14}H_4,\ NO_4,\ O_5$) and oxalic acids are formed.

Helicoidin ($C_{52}H_{34}O_{28}$, 3 Aq = $C_{26}H_{18}O_{14}$, $C_{26}H_{16}O_{14}$, 3 Aq) is a crystalline compound which is the result of the imperfect oxidation of salicin. It is prepared in the same manner as helicin, but the specific gravity of the nitric acid employed must not exceed 1·09.

Both chlorine and bromine form compounds with helicin, in which 1 equivalent of hydrogen is displaced by an equivalent of chlorine or of bromine, the formula of chlorohelicin being $C_{26}H_{15}ClO_{14}$: it is decomposed by emulsin into glucose and chloride of salicyl.

Nature of Salicin.—The foregoing observations and experiments appear to lead definitely to the conclusion that salicin must be regarded as a colligated body derived from saligenin and grape sugar. Saligenin is a substance which readily undergoes transformations by chemical agents, being converted by sulphuric acid into a peculiar red compound, by nitric acid into carbazotic acid, and by other oxidizing agents into oil of spiræa. When salicin is submitted to the action of chemical agents, the saligenin is the constituent which is first affected if these agents act with moderate intensity; whilst the sugar either remains in combination with the modified saligenin, as in the various forms of chlorosalicin, or it is set at liberty. If the reaction be more violent, the elements of the sugar also take part in the changes which are effected: for example, when salicin is oxidized by chromic acid, the saligenin yields the oil of spiræa, and the sugar produces formic acid.

(1235) *Populin* [$C_{40}H_{22}O_{16}$, 4 Aq=$C_{26}H_{17}(C_{14}H_5O_2)O_{14}$, 4 Aq]. —This compound may be regarded as salicin, in which one equivalent of hydrogen has been displaced by benzoyl. It is found in the bark and the leaves of the aspen (*Populus tremula*), and probably also in other varieties of the poplar. It is extracted by a process similar to that employed for salicin. Populin requires about 70 parts of boiling water for its solution, and 2000 parts of cold water; it is freely soluble in boiling alcohol. When crystallized from a hot aqueous solution it forms colourless, silky, extremely delicate needles, which have a sweetish taste resembling that of liquorice; these crystals, if heated to 212°, lose 4 equivalents of water; at a higher temperature they are decomposed, benzoic acid being amongst the products. When boiled with baryta water for a few minutes, a clear solution is obtained, and on separating the excess of baryta by means of a current of carbonic acid, the solution is found to contain salicin and benzoate of baryta:—

$$\overbrace{C_{40}H_{22}O_{16}}^{\text{Populin,}} + HO, BaO = \overbrace{BaO, C_{14}H_5O_3}^{\text{Benzoate of Baryta.}} + \overbrace{C_{26}H_{18}O_{14}}^{\text{Salicin.}}.$$

When boiled with dilute acids populin is decomposed into a mixture of benzoic acid, saliretin and glucose:—

$$\overbrace{C_{40}H_{22}O_{16}}^{\text{Populin.}} + 4\,HO = \overbrace{HO,\,C_{14}H_5O_3}^{\text{Benzoic Acid.}} + \overbrace{C_{14}H_6O_2}^{\text{Saliretin.}} + \overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}.$$

Synaptase is without action upon populin: concentrated nitric acid converts it into a mixture of nitrobenzoic, carbazotic and oxalic acids: dilute nitric acid converts it into *benzoylhelicin*, $C_{26}H_{15}(C_{14}H_5O_2)O_{14}$. A mixture of bichromate of potash and sulphuric acid liberates oil of spiræa from populin in abundance.

(1236) *Coumarin* ($C_{18}H_6O_4$).—This substance is found in the Tonka bean (*Coumaroma odorata*), in the common melilot, in the sweet scented vernal grass, to which much of the fragrance of hay is owing, and in several other sweet scented plants. Coumarin is most easily extracted from the Tonka bean by digesting the powdered seeds in alcohol; on evaporating the alcoholic solution, crystals of coumarin are obtained, and may be purified by digestion with animal charcoal, and by recrystallization. Coumarin assumes the form of colourless rectangular plates, or of rhombic prisms with slightly rounded faces. It melts at 122°, and boils at 518°; at which temperature it may be distilled unaltered. Its vapour has an agreeable aromatic odour. It has a burning taste, and is but slightly soluble in cold water, though it is freely dissolved by boiling water; the solution on cooling deposits coumarin in silky needles. Dilute acids dissolve it without alteration. Concentrated nitric acid converts it at first into *nitrocoumarin* ($C_{18}H_5(NO_4)O_4$), but by prolonged boiling it transforms it into carbazotic acid. Substitution compounds containing chlorine and bromine may also be formed from it. One of its most singular compounds is obtained by heating coumarin with a solution of perchloride of antimony in hydrochloric acid: gas is evolved, and, as the liquid cools, a canary-yellow precipitate ($C_{18}H_6O_4$, $SbCl_3$) is deposited in crystals.

When coumarin is boiled with a concentrated solution of hydrate of potash it assimilates the elements of water, and is converted into *coumaric acid*, which combines with the potash:—

$$\overbrace{C_{18}H_6O_4}^{\text{Coumarin.}} + KO,\,HO = \overbrace{KO,\,C_{18}H_7O_5}^{\text{Coumarate of Potash.}}.$$

Coumaric acid crystallizes in brilliant transparent plates, which may be obtained by decomposing a hot solution of coumarate of potash by hydrochloric acid. It fuses at about 374°; at a higher temperature it is decomposed, yielding a crystalline sublimate, and an oil which combines with potash, and reddens the persalts of iron.

When coumaric acid is fused with hydrate of potash, it is decomposed into acetate and salicylate of this base (Chiozza), whilst hydrogen escapes :—

$$\overbrace{HO, C_{18}H_7O_5}^{\text{Coumaric Acid.}} + 2(KO, HO) = \overbrace{KO, C_4H_3O_3}^{\text{Acetate of Potash.}} + \overbrace{KO, C_{14}H_5O_5}^{\text{Salicylate of Potash.}} + 2H.$$

5. *Oil of Aniseed.—Anisic Series.*

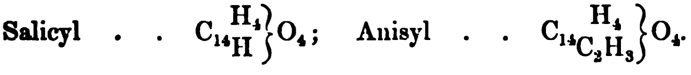
(1237) The essential oil furnished by the seeds of *Pimpinella anisum*, or common anise, of the *Anethum fœniculum*, or fennel, of the *Illicium anisatum*, or star anise, and of the *Artemisia dracunculus* or tarragon, are closely allied to each other; they vary in odour, but all consist of two portions, one of which is a hydrocarbon isomeric with oil of turpentine, and the other is a solid crystalline oxidized compound ($C_{20}H_{12}O_2$), which is convertible by oxidation into hydride of anisyl ($C_{16}H_7O_4$, H).

Solid Essence of Aniseed ($C_{20}H_{12}O_2$); *Sp. gr. of solid* 1·014; *of vapour* 5·19.—The crude essence of aniseed contains nearly four-fifths of its weight of this oxidized compound; which may be separated by exposing the oil to a low temperature, submitting the magma to pressure between folds of filtering paper, and crystallizing the residue from hot alcohol (sp. gr. 0·850). The solid essence thus obtained fuses at 65°, and boils at 432°. This substance when treated with chlorine or with bromine yields substitution compounds.

When essence of aniseed is mixed with concentrated oil of vitriol it is dissolved, and a red solution is formed; on the addition of water this solution is decomposed, and a substance termed *anisoine*, isomeric with the solid essence, is precipitated in white resinoid masses. A similar change is produced by treating the essence with bichloride of tin or with terchloride of antimony. This modification is insoluble in alcohol, but is soluble in ether and the essential oils: it is rather heavier than water, and is fusible above 212°. The oils of tarragon and of bitter fennel appear each to contain a distinct compound which is isomeric with anisoine and with the solid portion of oil of anise; the principal portion of essence of tarragon consisting of a modification which boils at 403°, and requires a low temperature for its solidification. These bodies, when oxidized, yield anisic acid, and other products which are identical with those furnished by oil of aniseed. Oil of cummin is also isomeric with the solid essence of anise, but the products of its oxidation are different (1217).

If oil of aniseed be heated in a sealed tube to 430°, in contact with a mixture of hydrate of soda and lime, a small quantity of an acid is formed, which is isomeric with cuminic acid, but not identical with this compound.

The action of nitric acid upon oil of aniseed gives rise to a series of compounds which have been particularly examined by Cahours. They present a close analogy with the compounds of the salicylic series. They may be regarded as containing a radicle termed *anisyl* ($C_{16}H_7O_4$), which may be viewed as a homologue of salicyl, or as a body in which one equivalent of hydrogen has been displaced by an equivalent of methyl; thus—



$$\text{Salicyl} \quad . \quad . \quad C_{14}\left.\begin{matrix}H_4\\H\end{matrix}\right\}O_4; \quad \text{Anisyl} \quad . \quad . \quad C_{14}\left.\begin{matrix}H_4\\C_2H_3\end{matrix}\right\}O_4.$$

The principal members of the anisic group are—

Hydride of anisyl	$C_{16}H_7O_4$, H
Anisic acid	HO, $C_{16}H_7O_4$, O
Chloride of anisyl	$C_{16}H_7O_4$, Cl
Anisine	$C_{48}H_{24}N_2O_6$.

(1238) *Hydride of Anisyl* ($C_{16}H_7O_4$,H); *Sp. gr.* 1·09.—When oil of aniseed is acted upon by dilute nitric acid a reddish oil is obtained, consisting of a mixture of anisic acid and hydride of anisyl. A quantity of oxalic acid is always formed during its preparation, which may be explained by the following equation:—

$$\overbrace{C_{20}H_{12}O_2}^{\text{Essence of Anise.}} + 12\,O = \overbrace{C_{16}H_7O_4, H}^{\text{Hydride of Anisyl.}} + \overbrace{2\,HO, C_4O_6}^{\text{Oxalic Acid.}} + 2\,HO.$$

If the oil thus obtained be washed with a weak solution of potash, in order to remove anisic acid, and be then cautiously distilled, the hydride passes over in the form of an amber-coloured liquid, which has an aromatic odour resembling that of new hay. Hydride of anisyl is homologous with oil of spiræa. It boils at about 490°; it is freely soluble in alcohol and in ether, but insoluble in water. Sulphuric acid dissolves it and forms a dark red liquid, from which on dilution with water the oil is separated unaltered. Hydride of anisyl forms crystalline compounds with the bisulphites of the alkalies.

Ammonia converts the hydride of anisyl into *anishydramide*, $3\,(C_{16}H_8O_4) + 2\,H_3N = (C_{48}H_{24}N_2O_6) + 6\,HO$. If anishydramide be maintained for two hours at a temperature of 330° or 340°, it fuses and becomes converted into an isomeric base, termed *anisine*. This body is soluble in alcohol, but scarcely soluble in water or in ether. Its alcoholic solution has a strong alkaline reaction and a bitter taste; it deposits the alkali in colourless prisms. The salts of this base may be obtained in crystals.

(1239) *Anisic Acid* ($HO, C_{16}H_7O_5$).—This substance is isomeric with salicylate of methyl, and has the composition of a homologue of salicylic acid. It may be obtained by boiling oil of anise with nitric acid (of sp. gr. 1·20); a yellow resinous mass termed *nitraniside* ($C_{20}H_{10}(NO_4)_2O_2$) is thus formed, and the liquid on cooling deposits long, colourless, brilliant prisms of anisic acid. This acid is scarcely soluble in cold water, but is freely soluble in boiling water, and in alcohol, and ether. It melts at 347°, and may be sublimed unaltered, condensing in white needles; boiling concentrated nitric acid converts it into *nitranisic acid* ($HO, C_{16}H_6NO_4, O_5$). The anisates are monobasic; those of the alkalies and of the earths are soluble and crystallizable: but those of lead, silver, and mercury are insoluble in cold water.

Chloride of Anisyl ($C_{16}H_7O_4, Cl$), *Sp. gr.* 1·261, is a colourless oil of a penetrating powerful odour; it is procured by distilling anisic acid with perchloride of phosphorus. It boils at 504°.

(1240) *Anisole* ($C_{14}H_8O_2$); *Sp. gr.* 0·991.—If anisic acid be distilled with an excess of caustic baryta, it yields a compound termed *anisole*, or *phenomethole*:—

$$\overbrace{HO, C_{16}H_7O_5}^{\text{Anisic Acid.}} + 2\,BaO = 2\,(BaO, CO_2) + \overbrace{C_{14}H_8O_2}^{\text{Anisole.}}.$$

Anisole has the composition of phenate of methyl ($C_2H_3O, C_{12}H_5O$). Cahours has obtained it synthetically by decomposing iodide of methyl with phenate of potash (1324):—

$$\overbrace{C_2H_3I}^{\text{Iodide of Methyl.}} + \overbrace{KO, C_{12}H_5O}^{\text{Phenate of Potash.}} = KI + \overbrace{C_2H_3O, C_{12}H_5O}^{\text{Anisole.}}.$$

Anisole is a colourless liquid of an aromatic odour; it boils at 306°, and is soluble in water as well as in alcohol and ether. When treated with fuming nitric acid, substitution compounds are obtained, which may contain 1, 2, or 3 equivalents of peroxide of nitrogen. *Nitranisole* ($C_{14}H_7NO_4, O_2$), when treated with an alcoholic solution of hydrosulphate of ammonia, yields a base termed *anisidine* ($C_{14}H_9NO_2$), whilst sulphur is deposited; and if *dinitranisole* be similarly treated, a nitrous base, *nitranisidine*, is obtained:—

$$\overbrace{C_{14}H_6\,(NO_4)_2O_2}^{\text{Dinitranisole.}} + 6\,HS = \overbrace{C_{14}H_8\,(NO_4)NO_2}^{\text{Nitranisidine.}} + 4\,HO + 6\,S.$$

Nitranisidine crystallizes in long brilliant needles, which are of a reddish brown colour: it forms well defined, crystallizable salts with sulphuric, nitric, and hydrochloric acids. If *trinitranisole* ($C_{14}H_5(NO_4)_3O_2$) be treated with hydrosulphate of ammonia, it yields a third base, *dinitranisidine* ($C_{14}H_7(NO_4)_2NO_2$), the salts of which, however, are very unstable, and are decomposed by contact with water. Nitranisidine when treated with the chlorides of benzoyl, of cinnamyl, and of cumyl, yields new compounds, in which benzoyl, cinnamyl, and cumyl are substituted for hydrogen, and compounds analogous to benzamide are produced; for example:—

$$\overbrace{C_{14}H_8NO_4,\ NO_2}^{\text{Nitranisidine.}} + \overbrace{C_{14}H_5O_2,\ Cl}^{\text{Chloride of Benzoyl.}} = \overbrace{C_{14}H_7,\ C_{14}H_5O_2,\ NO_4,\ NO_2}^{\text{Benzonitranisamide.}} + HCl.$$

Experiments of this nature present an interest in connexion with the question of the artificial formation of the natural organic bases; the empirical formula of benzonitranisamide ($C_{28}H_{12}N_2O_8$), presenting considerable resemblance to that of some of the natural alkaloids.

(*C.*) *Essential Oils which contain Sulphur.*

(1241) THE ALLYL SERIES.—The basis of all the oils of the sulphuretted essences which have been accurately examined is the hydrocarbon termed allyl (C_6H_5). Oil of garlic is a mixture of oxide with sulphide of allyl; and the oils of onions, and of assafœtida, and many of the *asphodeleæ* and *cruciferæ* yield similar oils; the essential oils of mustard, of horse-radish, and of scurvy grass consist chiefly of sulpho-cyanide of allyl.

The allyl series has recently been invested with new interest by the labours of Berthelot and De Luca, who have succeeded in preparing the *iodide of allyl*, or iodized propylene, as they term it, by decomposing glycerin with biniodide of phosphorus (1147); a discovery which in the hands of these chemists (*Comptes Rendus*, Feb. 4, 1856), and in those of Hofmann and Cahours (*Proceedings Roy. Soc.*, Feb. 7, 1856) has led to the formation of numerous derivatives of allyl, and has demonstrated the intimate connexion of these compounds with acrolein and the products of its oxidation. It will be necessary briefly to describe some of the compounds of this series. Hofmann and Cahours have indicated this connexion by calling the series the *acrylic* series; but, probably, most chemists will prefer to apply the older and less ambiguous term. In the description which follows they will therefore be denominated by terms indicative of their relation to allyl.

(1242) *Allyl* (C_6H_5, C_6H_5) *Sp. gr. of liquid* 0·684; *of vapour* 2·92.—When iodide of allyl is treated with sodium it is decomposed, iodide of sodium is formed, and allyl is liberated in the orm of a very volatile liquid, possessed of a peculiar penetrating odour, resembling that of radishes. It boils at 138°, emitting a vapour which burns with a very luminous flame. It is miscible with sulphuric acid, the mixture being attended with great elevation of temperature, and on standing for a few hours it gradually separates in a modified condition.

Allyl is immediately attacked by chlorine, bromine, and iodine, with which it forms compounds to which the formulæ $C_6H_5Cl_2$, $C_6H_5Br_2$, and $C_6H_5I_2$, have been assigned. It is, however, probable that these bodies are not true compounds of allyl with two equivalents of the halogen, but substitution products, perhaps of the form C_6H_4Cl, HCl, analogous to Dutch liquid. This point could be ascertained by examining the action of potash upon them.

(1243) *Allylic Alcohol* (C_6H_5O, HO).—When iodide of allyl is digested with oxalate of silver, violent action takes place, double decomposition occurs, in consequence of which oxalate of allyl, and iodide of silver are produced :—

$$\overbrace{2\,(C_6H_5I)}^{\text{Iodide of Allyl.}} + \overbrace{2\,AgO, C_4O_6}^{\text{Oxalate of Silver.}} = 2\,AgI + \overbrace{2\,C_6H_5O, C_4O_6}^{\text{Oxalate of Allyl.}}.$$

The oxalate of allyl or allyl-oxalic ether, is an aromatic liquid which boils at 404°: when treated with ammonia it yields oxamide, and allylic alcohol :—

$$\overbrace{2\,C_6H_5O, C_4O_6}^{\text{Oxalate of Allyl.}} + 2\,H_3N = \overbrace{2\,(C_6H_5O, HO)}^{\text{Allylic Alcohol.}} + \overbrace{(H_2N)_2C_4O_4}^{\text{Oxamide.}}.$$

Allylic alcohol is polymeric with acetone, and with propylic aldehyd, but it differs from them in properties. It mixes with water in all proportions : it is inflammable, and burns with a luminous flame. When treated with potassium, hydrogen is evolved, and *potassium-allyl-alcohol* (C_6H_5O, KO) is obtained in the form of a gelatinous mass.

Allylic alcohol when mixed with sulphuric acid unites with it, and forms *sulphallylic* acid (HO, C_6H_5O, S_2O_6) which corresponds with the sulphethylic. It is the vinic acid of the series.

(1244) *Oxide of Allyl; Allylic ether* (C_6H_5O, C_6H_5O).—When the compound of potassium with allylic alcohol is mixed with iodide of allyl, violent action occurs ; iodide of potassium is formed, and allylic ether is produced, by a decomposition analogous to that which attends the formation of ordinary ether when sodium-alcohol is treated with iodide of ethyl, (p. 150.)

$$\overbrace{\left.\begin{matrix}C_6H_5\\ I\end{matrix}\right\}}^{\text{Iodide of Allyl.}} + \overbrace{\left.\begin{matrix}C_6H_5\\ K\end{matrix}\right\}O_2}^{\text{Potassium Allyl Alcohol.}} = \left.\begin{matrix}K\\ 1\end{matrix}\right\} + \overbrace{\left.\begin{matrix}C_6H_5\\ C_6H_5\end{matrix}\right\}O_2}^{\text{Allylic Ether}}$$

Berthelot and De Luca state that oxide of allyl may also be formed by distilling iodide of allyl with red oxide of mercury. It is lighter than water, has an ethereal odour resembling that of radishes, and boils between 185° and 190°.

Oxide of allyl appears to exist ready formed in small quantity in oil of garlic, and in some other oils which resemble it. Wertheim also states that it may be obtained by decomposing oil of mustard by distillation in a closed tube with hydrate of soda and lime, but the decomposition of the sulphocyanide of allyl thus effected is slow and imperfect. It enters into direct combination with nitrate of silver, and forms a compound (C_6H_5O, AgO, NO_5) which may be obtained by mixing rectified essence of garlic with an excess of a concentrated alcoholic solution of nitrate of silver: in the course of twenty-four hours a black deposit of sulphide of silver is formed; the liquid must be boiled, and filtered; on cooling, the compound of oxide of allyl with nitrate of silver crystallizes in brilliant colourless radiated prisms, which are freely soluble in water, but sparingly so in cold alcohol. If this body be dissolved in ammonia, oxide of allyl is set at liberty.

A double allylic ether has also been formed by decomposing iodide of allyl by an alcoholic solution of potash; in which case *allyl-ethylic ether* (C_6H_5O, C_4H_5O), a liquid which boils at 144°·5 is produced. *Allyl-amylic ether* (C_6H_5O, $C_{10}H_{11}O$) may be obtained by substituting a solution of potash in fousel oil for the alcoholic solution of potash used in the previous experiment. It boils at 248°.

Hofmann and Cahours have obtained the same compounds by decomposing potassium-allyl-alcohol by iodide of ethyl, and by iodide of amyl.

(1245) *Chloride of Allyl* (C_6H_5Cl) is readily obtained by distilling allylic alcohol with chloride of phosphorus, and the *bromide* (C_6H_5Br) may be obtained with equal facility by distilling the alcohol with bromide of phosphorus.

(1246) *Iodide of Allyl; Iodized propylene* (C_6H_5I); *Sp. gr. of liquid* 1·789.—This interesting compound is obtained by the action of equal parts of biniodide of phosphorus and glycerin upon each other (1147). It is a colourless liquid, insoluble in water, but soluble in alcohol and in ether; it has an ethereal, somewhat alliaceous odour; when exposed to air and light it rapidly becomes brown; it boils at 214°, and may be distilled unaltered. Iodide of allyl is decomposed by digestion with an aqueous solution of ammonia, and on distillation with potash a volatile base of a fishy ammoniacal odour is formed, probably *allylia* ($C_6H_7N = C_6H_5, H_2N$).

(1247) *Sulphide of Allyl* (C_6H_5S).—This compound is contained in various essential oils, particularly in those of garlic, of onions, of leeks, of cress, of radishes, and of assafœtida.

Essence of Garlic.—When the cloves of garlic are distilled with water, a brown heavy fœtid oil passes over, constituting little more than 0·2 per cent. of the fresh root. It is partially decomposed by redistillation by an open fire, but if rectified from a bath of salt water about two-thirds of the oil may be obtained in the form of a yellowish liquid which is lighter than water, and which, when treated with chloride of calcium, and subsequently distilled from fragments of potassium, furnishes pure sulphide of allyl. The crude oil appears to contain portions of oxide of allyl, and of a higher sulphuretted compound of allyl which becomes decomposed during the distillation.

The *essence of assafœtida* contains a larger proportion of sulphur than that of garlic; it spontaneously evolves sulphuretted hydrogen, and cannot be redistilled without undergoing decomposition.

Sulphide of allyl is a colourless oil which is lighter than water; it has a high refracting power; its odour is less repulsive than that of crude oil of garlic. It may be distilled without undergoing decomposition; concentrated nitric acid converts it into formic and oxalic acids, whilst the sulphur is oxidized. Cold sulphuric acid dissolves it with a purple tint, but the oil is separated unaltered on dilution. It is rapidly dissolved by hydrochloric acid, and the mixture acquires a deep blue colour which disappears on the addition of water. Solutions of the alkalies do not decompose the sulphide of allyl.

Sulphide of allyl causes a precipitate in many metallic solutions, such as those of silver, mercury, gold, platinum, and palladium, but it does not precipitate the salts of lead or of copper. The nitrate of silver gradually decomposes it, sulphide of silver being formed, and the compound of oxide of allyl and nitrate of silver (1244) is produced. A peculiar sulphuretted compound of allyl with chloride of mercury is obtained by mixing alcoholic solutions of the sulphide of allyl and of corrosive sublimate; an abundant white precipitate is formed ($C_6H_5S, 2\,HgS + C_6H_5Cl, 2\,HgCl$). When this compound is distilled with sulphocyanide of potassium it is decomposed, and oil of mustard mixed with sulphide of allyl is amongst the products :—

$$(C_6H_5S, 2\,HgS + C_6H_5Cl, 2\,HgCl) + \overbrace{3\,(K, C_2NS_2)}^{\text{Sulphocy. Potass.}} = 3\,KCl + 2\,HgS + \overbrace{2\,(Hg, C_2NS_2)}^{\text{Sulphocy. Merc.}} + \overbrace{C_6H_5S}^{\text{Essence of Garlic.}} + \overbrace{C_6H_5, C_2NS_2}^{\text{Essence of Mustard.}};$$

in this reaction the double chloride of mercury and allyl is alone acted upon by the sulphocyanide, chloride of potassium and sulphocyanide of mercury being formed, whilst the sulphide of allyl passes over unaltered, accompanied by the oil of mustard, leaving sulphide of mercury in the retort.

(1248) *Essence of Mustard; Sulphocyanide of Allyl* (C_6H_5, C_2NS_2) : *Sp. gr. of liquid* 1·010 ; *of vapour* 3·54.—This compound constitutes the principal portion of the essential oil of mustard, from which it may be obtained in a state of purity by simple redistillation ; this operation frees the essence from a brown resinous matter with which it is usually contaminated. The pungency of the horseradish, of the scurvy grass, and of one or two other allied plants is also due to the sulphocyanide of allyl. Berthelot and De Luca made the interesting observation that when iodide of allyl is distilled with sulphocyanide of potassium, an oil is formed identical with essence of mustard—an observation which afforded the first indication of the intimate relation subsisting between the allylic series and that of glycerin :—

$$\overbrace{C_6H_5I}^{\text{Iodide of Allyl.}} + \overbrace{K, C_2NS_2}^{\text{Sulphocy. Potass.}} = \overbrace{C_6H_5, C_2NS_2}^{\text{Essence of Mustard.}} + KI.$$

The seeds both of the black and of the white mustard yield by expression a large quantity of a bland fixed oil, but they do not contain any essential oil ready formed ; white mustard does not yield the sulphocyanide of allyl.* The black mustard, how-

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* According to Babo and Hirschbrunn, white mustard contains the hydro-sulphocyanate of a peculiar alkali, termed *sinapine*, $C_{32}H_{23}NO_{10}$. This base, when acted upon by potash or soda, is decomposed into *sinapic* acid, and a new alkali, termed *sinkaline*, in the manner represented in the following equation, adopting the altered formula $C_{32}H_{23}NO_{10}$ proposed by Gerhardt :—

$$\overbrace{C_{32}H_{23}NO_{10}}^{\text{Sinapine.}} + 2(KO,HO) = \overbrace{2\,KO, C_{22}H_{10}O_8}^{\text{Sinapate of Potash.}} + \overbrace{C_{10}H_{13}NO_2}^{\text{Sinkaline.}} + 2\,HO.$$

An aqueous solution of sinapine has an intense yellow colour. Sinapine cannot be isolated in a pure condition owing to the facility with which it is decomposed : it forms crystallizable salts. The hydro-sulphocyanate is extracted from white mustard, after treating the dried flour successively with ether and absolute alcohol to remove the fixed oil and colouring matter, and then boiling the residue in alcohol of sp. gr. 0·825. After the solution has been ever, contains the potash salt of a compound termed *myronic acid*, which is susceptible of a decomposition analogous to that experienced by amygdalin. This decomposition is not effected until the crushed seed is moistened with water, a peculiar azotised ferment contained in the seed, and analogous to the synaptase of the almond, is thus brought into action, and the essential oil is developed. The composition of myronic acid is not known.

The essence of mustard is a colourless oil of a burning and painfully penetrating odour, which produces a copious flow of tears. If the essence be applied to the surface of the body, it speedily raises a blister upon the part. Essence of mustard is soluble in all proportions in alcohol, and in ether, but very sparingly so in water: if exposed to the air it absorbs oxygen and becomes brown. The purified essence boils at 298°; when hot it dissolves both sulphur and phosphorus in considerable quantities, but, as the solutions cool, these bodies are again deposited in crystals. Oil of mustard can be converted into essence of garlic by heating it for some hours in a sealed tube, with sulphide of potassium, at a temperature of 250°:—

$$\overbrace{2\,(C_6H_5,\ C_2NS_2)}^{\text{Essence of Mustard.}} + 2\,KS = \overbrace{(C_6H_5S,\ C_6H_5S)}^{\text{Essence of Garlic.}} + \overbrace{2\,(K,\ C_2NS_2)}^{\text{Sulphocy. Potass.}}$$

(1249) Oil of mustard combines at once with ammonia, and forms a compound which enters into direct combination with acids like a true organic base; from its origin it has been termed *thiosinnamine*:—

$$\overbrace{C_6H_5,\ C_2NS_2}^{\text{Oil of Mustard.}} + H_3N = \overbrace{C_8H_8N_2S_2}^{\text{Thiosinnamine.}} \text{ or } \overbrace{H_3(C_6H_5)N_2,\ C_2S_2}^{\text{Sulphuretted Allylurea.}}.$$

Thiosinnamine is the urea of the allyl series, but it contains 2 equivalents of sulphur instead of 2 equivalents of oxygen. Sulphocyanide of allyl also unites with other bases, such as ethylia, aniline, and naphthalidine, and forms analogous compounds.

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sufficiently concentrated by evaporation, the salt is deposited in crystals as the liquid cools. If the solution of this salt be mixed with an alkali, it assumes an intense yellow colour, and on boiling the solution, and subsequently adding hydrochloric acid in slight excess, sinapic acid is deposited. If baryta water be used to decompose the salt of sinapine, the sinapic acid is precipitated as an insoluble sinapate of baryta, and sinkaline may be obtained from the solution. Sinapic acid crystallizes in prisms; it is sparingly soluble in cold water, very soluble in boiling alcohol, and insoluble in ether; it fuses at a temperature above 300°: nitric acid dissolves it, and produces an intense red colour.

Sinkaline may be obtained in deliquescent crystals, which absorb carbonic acid from the air; it is a powerful base, but readily undergoes decomposition. With bichloride of platinum it forms a magnificent double salt, which crystallizes in orange-coloured six-sided prisms ($C_{10}H_{12}NO_2$, HCl, $PtCl_2$ + 2 Aq).

If thiosinnamine be triturated with red oxide of mercury, water and sulphide of mercury are formed, and a new basic substance free from sulphur, termed *sinnamine*, is obtained :—

$$\overbrace{C_8H_8N_2S_2}^{\text{Thiosinnamine.}} + 2\,HgO = 2\,HgS + 2\,HO + \overbrace{C_8H_6N_2}^{\text{Sinnamine.}}$$

Oxide of lead produces a similar decomposition.

Sinnamine has been regarded as a compound ammonia, in which one equivalent of hydrogen has been displaced by allyl, and a second equivalent by cyanogen, thus :—

$$C_8H_6N_2 = \left.\begin{matrix} H \\ C_6H_5 \\ C_2N \end{matrix}\right\} N \text{; or } \textit{cyanallylia.}$$

Sinnamine is soluble in water, and may be obtained in prismatic crystals. It is a powerful base, and expels ammonia from its salts. It occasions precipitates in solutions of lead, of iron, and of copper. The oxalate of sinnamine is the only salt which crystallizes readily; solutions of sinnamine which contain an excess of acid impart a yellow colour to a slip of deal.

(1250) *Sinapoline* ($C_{14}H_{12}N_2O_2$).—This base is usually formed by digesting essence of mustard upon hydrated oxide of lead :—

$$2(C_8H_5NS_2) + 6(PbO, HO) = C_{14}H_{12}N_2O_2 + 4\,PbS + 2(PbO, CO_2) + 4HO;$$

but it may also be produced by the action of water upon allyl-cyanic ether, which will be immediately described. Sinapoline is a feeble base which crystallizes in brilliant greasy flakes from its solution in water: it fuses below 212°. Its aqueous solution occasions a precipitate in solutions of corrosive sublimate and of bichloride of platinum.

(1250 *bis*) Hofmann and Cahours have also obtained a variety of compound allylic ethers. The most interesting of these appear to be the oxalate and the cyanate. The *allyl-cyanic ether* or *cyanate of allyl* (C_6H_5O, C_2NO), is prepared by acting upon cyanate of silver with iodide of allyl; the heat generated by the reaction is sufficient to cause the distillation of the ether, whilst iodide of silver remains in the retort. A colourless liquid is thus obtained which boils at 190°; its vapour possesses an intensely penetrating odour, and produces a copious flow of tears. When this ether is gently warmed with a solution of ammonia it is dissolved, and the solution on evaporation deposits magnificent crystals of allylic urea :—

$$\overbrace{C_6H_5O,\ C_2NO}^{\text{Allyl-cyanic Ether.}} + H_3N = \overbrace{H_3(C_6H_5)N_2,\ C_2O_2}^{\text{Allyl-urea.}}.$$

A corresponding crystalline compound may be obtained if aniline be substituted for ammonia. When allyl-cyanic ether is treated with water, carbonic acid is eliminated, and the ether is slowly converted into ***sinapoline*** ($C_{14}H_{12}N_2O_2$), which by its production in this manner is shown to be *diallyl-urea*:—

$$\overbrace{2\,(C_6H_5O,\,C_2NO)}^{\text{Allyl-cyanic Ether.}} \;+\; 2\,HO \;=\; \overbrace{H_2(C_6H_5)_2N_2,\,C_2O_2}^{\text{Sinapoline.}} \;+\; 2\,CO_2.$$

(1251) *Allylia.*—Concentrated solution of potash decomposes allyl-cyanic ether; sinapoline is formed, and if the liquid be distilled, ***allylia***, a basic substance which boils between 356° and 374°, passes over, mixed with methylia and tritylia. Allylia is the volatile alkali of the allylic series, which corresponds to ethylia in the ethylic series:—

$$\overbrace{C_6H_5O,\,C_2NO}^{\text{Allyl-cyanic Ether.}} \;+\; 2\,(KO,\,HO) \;=\; \overbrace{C_6H_5,\,H_2N}^{\text{Allylia.}} \;+\; 2\,(KO,\,CO_2).$$

The following table gives a synoptic view of the principal compounds in the allylic series:—

Allyl	C_6H_5, C_6H_5
Allylic alcohol .	C_6H_5O, HO
Allylic ether .	C_6H_5O, C_6H_5O
Allyl-ethylic ether	C_6H_5O, C_4H_5O
Sulphide of allyl	C_6H_5S, C_6H_5S
Chloride of do.	C_6H_5Cl
Bromide of do.	C_6H_5Br
Iodide of do.	C_6H_5I
Sulphocyanide of do. . . .	C_6H_5, C_2NS_2
Sulphallylic acid	HO, C_6H_5O, S_2O_6
Allyl-oxalic ether	$2\,C_6H_5O, C_4O_6$
Allyl-oxamic ether	C_6H_5O, H_2N, C_4O_5
Allyl-carbonic ether	$2\,C_6H_5O, C_2O_4$
Allyl-acetic ether	$C_6H_5O, C_4H_3O_3$
Allyl-benzoic ether	$C_6H_5O, C_{14}H_5O_3$
Allyl-cyanic ether	C_6H_5O, C_2NO
Allylia . . .	C_6H_5, H_2N
Cyanallylia (sinnamine)	$(C_6H_5, C_2N, H)N$
Allyl-urea . .	$H_3(C_6H_5)N_2, C_2O_2$
Diallyl-urea (sinapoline)	$H_2(C_6H_5)_2N_2, C_2O_2$
Sulphallyl-urea (thiosinnamine)	$H_3(C_6H_5)N, C_2S_2$
Acrolein (acrylic aldehyd)	$C_6H_3O_2, H$
Acrylic acid .	$HO, C_6H_3O_3$.

§ II. Resins.

(1252) These substances are produced by certain families of plants in considerable abundance, and they are also very numerous. They have a considerable commercial value, and are extensively employed in the preparation of the different kinds of varnish. They are generally obtained by making incisions into the wood of trees which produce them, when they exude in the form of a viscid liquid, consisting of the resin in solution in the essential oil of the plant. In the majority of cases they are formed by the oxidation of the essential oils contained in the trees; hence it is not surprising that in many instances they have the composition of oxides of the hydrocarbon $C_{40}H_{32}$, or of a hydrocarbon derived from this, having lost a certain number of equivalents of hydrogen in exchange for an equal number of equivalents of oxygen.

As a class, the resins are insoluble in water, but they are soluble in alcohol, especially when heated with it; many of them may be obtained from this solution in crystals by evaporation. A considerable number of them possess acid characters, in which case their alcoholic solutions redden litmus. The acid resins combine with the alkalies, and remain soluble in alkaline leys; these solutions, when agitated, produce a lather like that furnished by soap, but they are not precipitated like ordinary soap on the addition of chloride of sodium. Like the essential oils, the natural resins are usually mixtures of two or more resins, which often admit of separation by their unequal solubility in different menstrua.

The resins are transparent or translucent brittle solids; they are insulators of electricity, and become negatively electric by friction; they fuse at a moderate temperature, are very inflammable, and burn with a white smoky flame. If heated in close vessels they undergo decomposition, and yield various forms of hydrocarbon.

Common rosin is thus found to furnish the following products among others which have been less perfectly investigated :—

Hydrocarbons.	Formulæ.	Boiling point. °F.	Specific Gravity.	
			Liquid.	Vapour.
Terebene . .	$C_{20}H_{16}$	320°	0·86	4·81
Colophene . .	$C_{40}H_{32}$	599°	0·94	
Resinein . .	$C_{40}H_{28}O_2$	482°		
Retinaphtha or Toluole.	$C_{14}H_8$	226°	0·86	3·23
Retinyle or Cumole .	$C_{18}H_{12}$	302°	0·87	4·24
Retinole . .	$C_{32}H_{16}$	460°	0·90	7·11
Naphthalin . .	$C_{20}H_8$	428°		4·528
Metanaphthalin . .	$C_{40}H_{16}$?	617°		

(1253) *Common Rosin* or *Colophony.*—When ordinary turpentine is distilled with water, it leaves a residue of rosin amounting to from 75 to 90 per cent. of the turpentine employed. There are two principal kinds of rosin in the market, a brown and a white resin. The brown variety is furnished by the *Pinus abies*; it is an amber-coloured brittle solid, which consists of two distinct but isomeric resinous acids, the *sylvic* and *pinic* (HO, $C_{40}H_{29}O_3$; Laurent). Cold alcohol (sp. gr. 0·87) dissolves the pinic acid, which forms the larger proportion of the resin, and leaves it on evaporation as an amorphous mass. It may be purified from adhering traces of a neutral resin by precipitating its solution in cold alcohol by the addition of an alcoholic solution of acetate of copper. The pinate of copper thus precipitated may then be decomposed by any acid. When pinic acid is heated to partial decomposition, the residue in the retort is found to consist of another isomeric resinous acid, the *colopholic;* it neutralizes bases more perfectly than pinic acid, and is much less soluble in alcohol (Unverdorben).

The other constituent of rosin, *sylvic* acid, may be obtained from its solution in hot alcohol, in colourless rhombic prisms or plates, fusible at 260°. Its ethereal solution expels carbonic acid from the alkaline carbonates. It forms with oxide of lead a salt which crystallizes in slender four-sided needles.

White resin or *galipot* is obtained from Bordeaux turpentine, furnished by the *Pinus maritima,* and consists almost entirely of an acid resin, the *pimaric,* which is isomeric with the preceding. This acid may be extracted by removing from the powdered resin the substances which are soluble in a mixture of six parts of cold alcohol and one of ether: the residue, if treated with boiling alcohol, deposits pimaric acid as it cools. When the alcoholic solution of pimaric acid is evaporated, the acid is deposited in masses indistinctly crystallized. If this acid be melted and allowed to cool, it yields a colourless glass as clear as crystal: this melted resin when powdered is dissolved by an equal weight of alcohol, but the solution thus obtained, if left for a few minutes, suddenly begins to deposit elliptical crystals, which require for solution ten times their weight of alcohol, and possess all the properties of pimaric acid before fusion. Pimaric acid is freely soluble in ether. If it be distilled in vessels from which air is excluded, the distillate is found to consist principally of another isomeric resin, termed *pyromaric acid,* distinguished by forming with lead a salt which crystallizes in delicate needles. Pyromaric acid, according to Gerhardt, is identical with sylvic acid.

Ordinary rosin is dissolved completely by alkaline leys: it enters largely into the formation of yellow soap.

If nitric acid be boiled upon ordinary rosin the compound is oxidized and dissolved, and on evaporating the solution to the consistence of a syrup, it deposits when left to itself for some weeks small four-sided prisms with an oblique terminal face. This substance is named *terebic acid* ($HO, C_{14}H_9O_7$). It is sparingly soluble in cold water, but much more soluble in boiling water, as well as in alcohol and ether; it requires a high temperature for its fusion, and is decomposed at about 400°.

(1254) *Varnishes.*—The resins most extensively employed in the preparation of the different kinds of varnish are those of copal (from the *Hymenæa verrucosa ?*), mastich (from the *Pistachia lentiscus*), sandarach (from the *Juniperus communis*), lac, and occasionally those of elemi and anime. Copal is a hard, nearly colourless, transparent resin, which is dissolved with difficulty in the state in which it is imported; but if powdered and exposed to the air for some weeks, or if fused so as to enable it to absorb oxygen, it is more readily attacked by solvents.

The solvents employed in preparing varnishes are oil of turpentine, wood naphtha, and spirit of wine; the resin before being added to the solvent must be pulverized, and afterwards mixed with broken glass in order to prevent the powder from agglutinating into lumps. When the varnish is spread over the surface of any object which it is intended to protect, the solvent evaporates and leaves a thin transparent coating of resin. The spirituous varnishes dry the most rapidly, but they are apt to crack and scale off. This defect is partially remedied in the turpentine varnishes, which dry more slowly; and it is still more effectually obviated in what are termed oil varnishes, in which a small quantity of some drying oil, such as that of linseed or of poppy, is added to the solution in rectified turpentine: these varnishes require a considerable time for complete hardening, but they are very durable. The common varnish used for oil paintings and maps consists of 24 parts of mastic, 3 of Venice turpentine, and 1 of camphor; these are mixed with 10 parts of pounded glass, and dissolved in 72 of rectified oil of turpentine.

(1255) Guaiacum resin is the exudation of the *Guaiacum officinale.* It is of a dark greenish-brown colour, and is readily pulverized. It has a taste which is at first slight, but afterwards becomes acrid and hot; its odour is feeble, but resembles that of benzoin. Alcohol dissolves the greater part of this resin; ether does not dissolve it so completely, and it is insoluble in the fixed oils. It is also freely soluble in a solution of potash and in oil of vitriol. The alcoholic tincture yields a blue precipitate when acted on by chlorine: with sulphuric acid it gives a green precipitate. White paper when stained with tincture of guaiacum acquires a pale yellow tint; and if this be exposed to the more refrangible rays of the solar spectrum, it becomes of a fine blue or greenish-blue colour. The pale yellow tint is restored when the altered paper is exposed in the less refrangible portion of the spectrum, or when a gentle heat is applied to it. This restoration of the colour depends upon the absorption of oxygen: powdered guaiacum when exposed to the air absorbs oxygen and becomes green. Fuming nitric acid dissolves the resin and acquires a green colour; if a certain quantity of water be added, a green precipitate is formed, and the solution becomes blue, but the addition of a larger quantity of water renders the precipitate blue and the solution brown.

Resin of guaiacum appears to consist of two distinct resinous acids, one of which, *guaiacic acid* ($HO, C_{12}H_7O_5$; Deville), may be obtained from its alcoholic solution, crystallized in beautiful needles, which are freely soluble in water.

Guaiacum resin melts at a moderate heat, and begins to undergo decomposition at about 600°. Amongst the products of its destructive distillation Deville enumerates three definite compounds:—1.—A light volatile oil, *guaiacene* ($C_{10}H_8O_2$) of sp. gr. 0·874: it boils at 244°, giving off a vapour of sp. gr. 2·92, and absorbs oxygen from the air, forming a beautiful crystalline compound. 2.—A volatile compound which crystallizes in pearly scales. And, 3.—An oil heavier than water, termed *hydride of guaiacyl* ($C_{14}H_8O_4$); this liquid boils at about 410°, emitting a vapour of sp. gr. 4·49. It is soluble in alcohol, ether, and acetic acid, but not in water.

(1256) Lac.—One of the most valuable of the resins is lac, which occurs in commerce under three distinct forms; viz., as *stick-lac*, *seed-lac*, and *shell-lac*. This resin exudes from the branches of several trees in tropical climates, and in particular from the *Ficus indica*, *Ficus religiosa*, and *Rhamnus jujuba*, in consequence of the punctures of the female of a small insect of the cochineal tribe, the *coccus ficus*; the resinous juice which exudes hardens over the insects. The young shoots when cut off, covered with the resin, and enclosing the cocci, constitute stick-lac. The crude stick-lac is then bruised, and the fragments of the branches are removed; after which the resinous mass is digested in a weak solution of carbonate of soda, by which means a red colouring matter contained in the insects is extracted. This material is now extensively used as a dye, and has largely displaced the more expensive cochineal. The residue which is insoluble in the alkaline ley, forms the commercial *seed-lac*. When this is melted, strained through a long cotton bag, and the viscous resin while soft compressed into flat sheets, between leaves or stones, it forms the scaly purified mass which is sold under the name of *shell-lac*. This resin appears to consist of a mixture of four or five distinct compounds, one of which is acid and may be obtained in crystals, and according to Unverdorben, it also contains both oleic and margaric (palmitic) acids.

Lac is extensively used as a stiffening for hats, and it forms the principal constituent of the better kinds of sealing-wax. Red sealing-wax owes its brilliant colour to vermilion; 48 parts of shell-lac, 12 of Venetian turpentine, and 1 part of balsam of Peru, melted at a gentle heat, and incorporated with 36 parts of vermilion, furnish red sealing-wax of the best quality (Löwig). When lac is mixed with half its weight of sandarach, and a small quantity of Venice turpentine, it forms with 10 or 12 parts of alcohol a varnish, technically termed *lacquer*, which is much employed for heightening the colour of brass and bronzed articles.

(1257) BALSAMS.—The soft viscous resins which consist of a large mixture of essential oil with the resin, are termed balsams; such, for example, as balsam of copaiba, and balsam of Canada. Some of them contain in addition benzoic or cinnamic acid, such as the balsams of benzoin, tolu, storax, and Peru.

Balsam of Copaiba is obtained from several species of *Copaifera*. It consists of a volatile essential oil isomeric with oil of turpentine; a resinous acid, *capivic acid* $C_{40}H_{30}O_4$, isomeric with pinic acid; and a viscous neutral resin. *Balsam of Canada* is the nearly colourless liquid resin of the *Pinus balsamea*.

(1258) GUM RESINS, are the milky juices of many plants, solidified by exposure to air. They consist chiefly of the peculiar resins and essential oil of the plants, mixed with a large proportion of gum; consequently they produce when rubbed up with water, a milky-looking liquid, or emulsion, the gum becoming dissolved, and retaining the resin and oil in suspension. Dilute alcohol dissolves the gum resins in great measure, as do also weak alkaline solutions. The gum resins form a numerous and important class of medicinal remedies. Ammoniacum, assafœtida, aloes, euphorbium, galbanum, gamboge, myrrh, olibanum, and scammony, all belong to this class of bodies.

(1259) AMBER.—Some fossil substances approach more closely to the resins than to any other class of compounds; of these, one of the most important is *amber*. It is a light-yellow transparent substance, with a density generally a little greater than that of water. Its property of becoming electric by friction is familiarly known. It occurs often in beds of wood coal, but is chiefly found after storms, on the coasts of the Baltic, between Königsberg and Memel. Amber consists of a mixture of several resinous bodies, which have not been accurately examined; about one-eighth of its weight is soluble in alcohol, and about one-tenth of it is soluble in ether. If heated in close vessels it melts, gives off succinic acid, water, and a peculiar empyreumatic oil, which consists of a mixture of several hydrocarbons having nearly the same composition as oil of turpentine. The succinic acid appears to be furnished solely by that portion of the resin which is soluble in ether (Schrötter). A small quantity of succinic acid exists ready formed in the resin, and can be extracted by digesting powdered amber in an alkaline solution. The empyreumatic oil is furnished principally by the bituminous portion, which is insoluble in ether and in alcohol. Amber, when treated with nitric acid, is gradually dissolved; succinic acid crystallizes from the solution when concentrated, and ordinary camphor is found in the distillate.

(1260) CAOUTCHOUC or *Indian-rubber* (xC_8H_7?): *Sp. gr.* from 0·92 to 0·96.—This substance occurs in small quantities in the juices of many plants, particularly of the *Urticaceæ*, *Euphorbiaceæ*, and *Apocynaceæ*. Its available supply, however, is the spontaneously solidified milky juice of the *Hævæa elastica*, *Jatropha elastica*, and some other tropical plants. As first procured by incisions into the stem of the plant, it appears as a yellowish milky fluid which, in addition to caoutchouc, contains albumen; the albumen occasions the juice on being boiled to coagulate. When the fresh juice is exposed to the air in thin films, it speedily dries and hardens into elastic layers of brownish yellow caoutchouc. The caoutchouc is not dissolved in the juice, but is merely suspended in it, and when the liquid is diluted with water it rises to the surface like cream; when once become coherent it cannot again be diffused through water. Commercial caoutchouc, from the mode of its preparation, retains the albumen and other constituents of the juice, but pure caoutchouc is a peculiar form of hydrocarbon (Faraday). In its solid condition it is extremely elastic, especially when warm. Although insoluble in water, it softens considerably in this liquid at the boiling temperature, and is thereby rendered more easily acted upon by its peculiar solvents. Alkaline solutions are without effect upon caoutchouc. Even chlorine attacks it very slowly; concentrated nitric and sulphuric acids decompose it, but when dilute they are entirely inert.

The proper solvents of caoutchouc are washed ether, chloroform, bisulphide of carbon, coal naphtha, and rectified oil of turpentine. In these liquids it first swells up very considerably, and eventually forms a ropy liquid, which on evaporation furnishes the caoutchouc with its original elasticity. This property is turned to account in the manufacture of various waterproof or "Macintosh" articles. According to Payen, caoutchouc consists of two portions, one of which is soluble in the liquids above mentioned, whilst the other portion merely softens and swells up, but does not undergo true solution. Caoutchouc is also dissolved by the fixed oils, but its elasticity is thereby destroyed. Waterproof cloth is prepared by varnishing one surface of a fabric constructed for the purpose with a solution of caoutchouc, and bringing it in contact with a second sheet similarly prepared, and passing the two together between rollers. The freshly cut edges or surfaces of a piece of caoutchouc cohere readily; this property, with its pliancy and elasticity, together with its power of resisting most chemical agents, renders it invaluable in the laboratory for forming flexible tubes and joints, used in connecting apparatus in a secure and air-tight manner. Caoutchouc melts at a heat of about 250° or 260°; after it has been melted it does not solidify on cooling, but forms a sticky mass which does not become solid even when exposed to the air for months. Owing to this property it furnishes a valuable material for the lubrication of stop-cocks, and joints intended to remain moveable yet air-tight. If caoutchouc be heated strongly in the open air it takes fire, and burns with a bright luminous flame.

If distilled in close vessels, caoutchouc furnishes a mixture of several different hydrocarbons. The most volatile of these has a sp. gr. of 0·654; it boils between 92° and 110°, and remains liquid at very low temperatures. Himly has given the name of *caoutchine* to a hydrocarbon of sp. gr. 0·842 in the liquid form, and 4·46 in that of vapour. It boils at 340°, and is isomeric with oil of turpentine; which it resembles in being miscible in all proportions with alcohol, ether, and the fixed and volatile oils. It may be exposed to a cold of — 22° without becoming solid. It dissolves caoutchouc freely.

Bouchardat found, among the less volatile portions of the oil, a yellow oily hydrocarbon, *heveène*, polymeric with olefiant gas. It had a sp. gr. of 0·921, and boiled at 599°. The same chemist likewise obtained during the distillation of caoutchouc a very volatile portion which required the application of a freezing mixture for its condensation; he describes the liquid thus obtained as a mixture of three hydrocarbons, one of which appeared to be identical with tetrylene (1021): the second, of sp. gr. 0·65, boiled at 58°, and when placed in a freezing mixture yielded crystalline plates fusible at 14°: this compound he termed *caoutchene*. The third compound was considered to be identical with Reichenbach's eupion (1310).

(1261) A highly valuable modification of caoutchouc, discovered by Goodyear, has lately been introduced into the arts under the name of *vulcanized* Indian rubber, which from its almost perfect elasticity at all temperatures below that of 240°, admits of a variety of useful applications. The cut edges of this form of caoutchouc do not cohere by pressure, and it does not become adhesive to other bodies at temperatures below 212°. Caoutchouc when immersed in the form of sheet in melted sulphur at 250° gradually imbibes from 12 to 15 per cent. of its weight of sulphur, but it does not at this temperature experience any change in its physical or chemical properties. If such sulphurized rubber be heated for a few minutes to about 300°, the peculiar elastic modification however is produced, and if the temperature be allowed to rise much higher than this, the mass first becomes black, hard and horny, and at a few degrees beyond this it is converted into a hard brittle substance, which at a higher temperature undergoes carbonization and decomposition. Vulcanized caoutchouc appears to consist of a combination of the elastic gum with 2 or 3 per cent. of its weight of sulphur. The excess of sulphur which is usually present is only mechanically distributed through the mass, and may be removed by the use of solvents, such as benzole or sulphite of soda. This excess of sulphur is injurious to the elasticity of the material, and gradually renders it brittle and rotten. Several modes of effecting the combination of sulphur with caoutchouc are employed. One of the most useful consists in dissolving the caoutchouc in turpentine in which the proper proportion of sulphur had been previously dissolved: on allowing the solvent to evaporate, the mixture of caoutchouc and sulphur is left endued with the properties of common caoutchouc, and may be easily moulded into the form of the various articles required; it is only on the application of a temperature ranging from 270° to 300° that the peculiar properties of the sulphurized compound are developed. The heat is most advantageously applied by exposing the articles to the direct action of high pressure steam at 270° or 280°. The addition of a certain proportion of carbonate of lead to the compound is found to produce an article better adapted for certain purposes, such as the manufacture of overshoes or goloshes, than one in which sulphur only is used; due proportions of sulphur and of the salt of lead are incorporated with the caoutchouc by causing the caoutchouc mixed with the other ingredients to pass repeatedly between polished hollow iron rollers maintained at a temperature of about 170°, by the injection of steam into their interior. Vulcanized Indian-rubber withstands prolonged digestion in naphtha or turpentine without undergoing solution.

(1262) GUTTA PERCHA.—This substance, which is similar in chemical properties to caoutchouc, was introduced into this country as an article of commerce about the year 1844. Gutta percha is the concrete juice of the *Isonandra percha*, a tree belonging to the family of the *Sapotaceæ*, which grows abundantly in Singapore, Borneo, and other islands of the Eastern archipelago. The name *percha* is that given by the Malays to the tree which produces it; it grows to a diameter of five or six feet, and though as timber it is valueless, the fruit yields an oil fit for food. On cutting notches through the bark into the wood, a milky juice exudes, which speedily solidifies. Gutta percha is a tough inelastic substance, which at ordinary temperatures retains any shape which may have been impressed upon it, but below 212° it becomes so soft that it may be moulded like wax, and indeed may be employed for taking casts and impressions, since it will copy the finest lines with fidelity; beautiful mouldings, and a variety of useful and ornamental articles are thus made with great facility. It also possesses the valuable property of welding together when in this soft condition, provided that the surfaces are quite free from any film of moisture. When cold it again becomes hard, and possessed of extraordinary tenacity. It is, when pure, of a pale brown colour, possessing a peculiar odour somewhat resembling that of caoutchouc. When rubbed it becomes negatively electric, and if dry it is an insulator of electricity; and this property has led to its extensive employment in the covering of wires for telegraphic purposes (260). It is also largely used as a waterproofing material, and is employed as a substitute for leather in soling boots and shoes. It furnishes a valuable material for the preparation of tubes for conveying liquids; it is likewise used as a substitute for leather in the construction of bands for driving machinery, and is daily receiving new and useful applications.

Gutta percha is quite insoluble in water; but it is dissolved readily by benzole, chloroform, bisulphide of carbon, turpentine, and the essential oils in general. If heated moderately it melts; and beyond this point is decomposed, yielding inflammable products. Solutions of the alkalies are without action upon gutta percha. Hydrochloric and dilute hydrofluoric acids, as well as the dilute acids in general, have no action upon it; hence it is employed in the preparation of bottles and vessels used for containing these liquids. The principal drawback to this use is the difficulty of preventing it from retaining a certain degree of porosity, which allows the slow transudation of liquids through its mass. Concentrated nitric acid rapidly attacks and disintegrates it, and oil of vitriol produces the same effect more gradually.

Payen states that purified commercial gutta percha consists of three distinct portions, the most abundant of these, the *pure gutta,* constitutes from 75 to 82 per cent. of the mass, and is insoluble in alcohol and in ether. It is believed that this substance is a hydrocarbon isomeric with caoutchouc. The other two constituents are a white and a yellow resin, both of which are soluble in boiling alcohol; but the white resin is nearly insoluble in this liquid when cold; by deposition from a hot alcoholic solution it may be obtained crystallized in pearly plates, disposed in radiated tufts. The yellow resin is amorphous.

(1263) RESIN OF JALAP.—This substance has been made the subject of numerous careful experiments. It may be obtained in a colourless form by treating the chopped roots of jalap with boiling water, repeatedly submitting them to pressure between each operation, and when the expressed liquid is no longer coloured, extracting the resin from the undissolved portion by means of boiling alcohol (sp. gr. 0·880). This resin amounts to from 10 to 15 per cent. of the weight of the root operated on. It is a mixture of two definite resins. One of these (*pararhodeoretin*) is soluble in ether, and is powerfully acid; it has the peculiar odour and acrid taste of jalap. It does not crystallize from its alcoholic or ethereal solutions, but if these be mixed with water, the semi-solid mass which is formed becomes gradually filled with needle-shaped crystals; it may be sublimed. According to the analysis of Johnston it may be represented as ($C_{40}H_{34}O_{18}$).

The resin which is insoluble in ether (*jalapin* or *rhodeoretin*) is remarkable for being susceptible of decomposition into glucose and a resinous acid. Jalapin is white, and destitute of odour and taste. It is fusible at 300°. Alcohol and acetic acid dissolve it readily. It is also readily soluble in alkaline solutions, especially if boiled with them. Mayer terms it *convolvulin,* and assigns to it the formula ($C_{62}H_{50}O_{32}$). This resin appears to constitute the purgative principle of the jalap. Oil of vitriol dissolves it slowly, and assumes a beautiful red colour, which gradually passes into brown. On dilution an oily looking acid body is precipitated, and glucose remains in solution. According to Mayer, the fusiform variety of jalap (*Convolvolus orizabensis*) contains a resin homologous with rhodeoretin ($C_{68}H_{56}O_{32}$), which when treated with sulphuric acid is similarly decomposed, glucose remaining in the solution.

§ III. GLUCOSIDES, OR COMPOUNDS WHICH CONTAIN GLUCOSE.

(1264) In the course of the present chapter some crystalline compounds have been described, which like amygdalin, salicin, and populin, under certain circumstances break up into glucose, and into some compound or compounds characteristic of the substance from which it is derived. The compounds which yield sugar when thus broken up, are termed *glucosides*. They may be subdivided into two classes: one of these consists of neutral substances, like amygdalin and salicin; the other consists of acid bodies, such as gallotannic acid. We shall now proceed to notice some of these compounds; viz., phloridzin, quercitrin, arbutin, esculin, and saponin.

(1265) PHLORIDZIN ($C_{42}H_{24}O_{20}$, 4 Aq; Strecker).—This is a substance which occurs in the bark of the apple, pear, cherry, and plum tree, and probably in other fruit trees. In order to extract it, it is sufficient to boil the bark for some time with water, and to allow the liquid to cool. Phloridzin is deposited in silky crystals, which may be purified by redissolving them in water, digesting with animal charcoal and recrystallizing. It has a slight bitter flavour, followed by a sweetish taste. It requires upwards of 1000 parts of cold water for solution, but it is largely soluble in boiling water. Alcohol and wood spirit dissolve it freely, but it is nearly insoluble in ether. Its alcoholic solution causes left-handed rotation in a ray of polarized light. When heated to 212° it loses four equivalents of water, and at a temperature between 223° and 228° it undergoes fusion, after which, by an additional elevation of temperature, without undergoing any further loss of water, it becomes solid, and does not melt again until the temperature has been raised to 320°. At 392° it again begins to give off water, and assume a red colour, forming a resinoid body ($C_{42}H_{20}O_{16}$), termed *rufin*; this substance is soluble in alcohol. Boiling water also dissolves it, but the solution is entirely colourless.

An aqueous solution of phloridzin yields a white precipitate with one of subacetate of lead (6 PbO, $C_{42}H_{24}O_{20}$?). It also forms compounds with baryta and lime, but these substances become brown by exposure to air.

Phloridzin, when boiled with weak acids, is decomposed into grape sugar, and a resinous matter termed *phloretin*:—

$$\overbrace{C_{42}H_{24}O_{20}}^{\text{Phloridzin.}} + 4\,HO = \overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}} + \overbrace{C_{30}H_{14}O_{10}}^{\text{Phloretin.}}.$$

Phloridzin, under the combined influence of air and ammonia, yields a red, bitter, uncrystallizable compound termed *phlorizein*,

($C_{42}H_{30}N_2O_{26}$), which is readily soluble in boiling water. When phloridzin is exposed to the vapour of ammonia, it produces a beautiful blue compound with a coppery lustre which appears to be a compound of phlorizein with ammonia; this substance is very soluble in water, and cannot be obtained in crystals; sulphuretted hydrogen and other deoxidizing agents destroy this blue colour, but it is restored by exposure to the air.

Phloridzin does not yield any essential oil when treated with chromic acid or other oxidizing agents; in this respect it presents an important difference from salicin, which in other points it greatly resembles.

(1266) **Quercitrin** ($C_{36}H_{18}O_{20} + 2\,Aq$).—This substance is homologous with phloridzin, and contains 3 (C_2H_2) less than this body. Quercitrin is the yellow, crystallizable colouring matter, contained in the bark of the quercitron or *Quercus tinctoria*. It may be extracted from the bark by means of alcohol, sp. gr. 0·84; the tannic acid is removed by the addition of gelatin, and the liquid on evaporation yields quercitrin, which may be purified by recrystallization from alcohol. It is sparingly soluble in boiling water and ether, but is readily dissolved by hot acetic acid, as well as by weak solutions of the alkalies, with which it forms a liquid of a greenish-yellow colour, which gradually passes into dark-brown. A solution of alum slowly developes a beautiful yellow colour in its solutions. Solutions of acetate of lead, acetate of copper, and chloride of tin, precipitate it in yellow flocculi. With persulphate of iron it produces an olive-green colour. When quercitrin is boiled with dilute sulphuric or hydrochloric acid, it is decomposed into glucose and *quercetin* ($C_{24}H_8O_{10}$), a substance sparingly soluble in water, but readily soluble in alcohol: it may be obtained in minute lemon-yellow crystals. Quercetin is also soluble in solutions of potash and of soda, to which it communicates a golden-yellow colour. The decomposition of quercitrin by acids may be thus represented:—

$$\overbrace{C_{36}H_{18}O_{20}}^{\text{Quercitrin.}} + 4\,HO = \overbrace{C_{24}H_8O_{10}}^{\text{Quercetin.}} + \overbrace{C_{12}H_{12}O_{12}, 2\,HO.}^{\text{Glucose.}}$$

(1267) **Arbutin** ($C_{32}H_{22}O_{19}$? Kawalier) is a crystallizable principle contained in the leaves of the *Arctostaphylos uva ursi*, which when treated with synaptase is decomposed into glucose, and a crystalline body termed *arctuvin* ($C_{20}H_{10}O_7$?):—

$$\overbrace{C_{32}H_{22}O_{19}}^{\text{Arbutin.}} + 2\,HO = \overbrace{C_{20}H_{10}O_7}^{\text{Arctuvin.}} + \overbrace{C_{12}H_{12}O_{12}, 2\,HO.}^{\text{Glucose.}}$$

(1268) **Esculin** or *polychrome* ($C_{42}H_{24}O_{26}$; at 212°).—This substance is contained in the bark of the horse-chesnut. In order to extract it, the aqueous infusion of the bark is treated with acetate of lead, and filtered, the excess of lead is removed by means of sulphuretted hydrogen, and the liquid is evaporated to the consistence of a syrup; in the course of a few days the esculin crystallizes: it may be washed with cold water, and recrystallized first from weak alcohol (sp. gr. 0·940) and afterwards from boiling water. Esculin forms small colourless needles, which have a bitter taste and a slightly acid reaction. It is sparingly soluble in cold water and in ether, but is dissolved abundantly by boiling water, and less freely by hot alcohol. Solutions of esculin are particularly remarkable for their fluorescent power, in consequence of which they appear in certain positions to be deep blue, although colourless if viewed by transmitted light. Acids destroy this property, but the addition of an alkali to the liquid heightens the fluorescent character. Esculin fuses and loses water when heated to 320°; at a higher temperature it is decomposed, emitting an odour of burnt sugar, whilst a small quantity of esculetin is sublimed in crystals.

Esculin when boiled with dilute acids, or when digested with synaptase, undergoes decomposition into esculetin and glucose:—

$$\overbrace{C_{42}H_{24}O_{26}}^{\text{Esculin.}} + 10\,HO = \overbrace{C_{18}H_{6}O_{8}}^{\text{Esculetin.}} + \overbrace{2\,(C_{12}H_{12}O_{12},\ 2\,HO)}^{\text{Glucose.}}.$$

Esculetin is a substance which has a slightly acid reaction upon litmus; it is sparingly soluble in cold water, in cold alcohol, and in ether; but it is freely soluble in boiling alcohol, which deposits it in crystalline needles or plates resembling those of benzoic acid. Esculetin is soluble in solutions of the alkalies, forming a golden yellow liquid; and a hot concentrated solution in ammonia, as it cools, deposits a yellow crystalline compound. The presence of a trace of a persalt of iron gives to esculetin a dark green tinge, but the colour is destroyed on the addition of an acid. A solution of acetate of lead when mixed with one of esculetin, produces a lemon yellow precipitate ($C_{18}H_{4}Pb_{2}O_{8}$).

(1269) *Saponin* ($C_{24}H_{20}O_{14}$?).—This substance is contained in a considerable number of plants, including the *Saponaria officinalis*, the *Polygala senega*, and the root of the common pink: it is also found in the pimpernel, in the fruit of the horse-chesnut, and in several varieties of *Lychnis*. Saponin is easily extracted by means of boiling alcohol (sp. gr. 840), from the root of the *Saponaria* or *soap-wort;* as the liquid cools the saponin is deposited as an amorphous sediment, which if coloured must be digested in ether, in order to remove the colouring matter.

When dry, saponin forms a colourless friable mass, which is destitute of odour, and of a sweetish, styptic, persistent taste. If applied to the mucous membrane of the nose it produces violent sneezing. Saponin is soluble in water in all proportions, yielding a somewhat opalescent liquid, which froths strongly on agitation, like a solution of soap, even though it may not contain more than a thousandth of its weight of saponin; the liquid when evaporated leaves the saponin in the form of a transparent, brittle varnish. Its solution, or an infusion of soap-wort, is sometimes employed instead of a solution of an alkaline soap, for cleansing the finer varieties of wool from grease. Saponin is also soluble in dilute alcohol, but insoluble in ether. Its solutions yield a white precipitate with subacetate of lead.

When boiled with dilute acids saponin yields a peculiar acid, the *saponic* or *esculic*, and at the same time a substance resembling gum ($C_{12}H_{11}O_{11}$), is separated (Rochleder and Schwartz). Saponic acid may also be obtained by digesting saponin in weak alkaline solutions. The composition of saponic acid is doubtful, but it presents well-marked characters. It is nearly insoluble in water and in ether, but is readily dissolved by alcohol, which deposits it in granular crystals. Its salts with potash, soda, and ammonia, are soluble in hot water, and the liquid on cooling sets into a jelly. A solution of these salts in dilute alcohol, sp. gr. 0·960, deposits them in pearly crystals. Saponic acid forms compounds with lime, baryta, copper, and lead, which are insoluble in water, but soluble in dilute alcohol.

A variety of other neutral crystallizable principles have been obtained from plants, many of which are used medicinally, but few of them have been minutely examined. It is probable that many of these bodies will prove to be identical with others already known, and many others will most likely be found to belong to the class of glucosides.

CHAPTER VIII.

COLOURING MATTERS.

(1270) THE substances which are about to be treated of in the present chapter under the head of *colouring matters*, are grouped together on account of the similarity in the modes of applying them in the arts, and not from any well-marked chemical relations which exist between them. The relations of many of these bodies to other groups are, however, remarkable, and present many points of considerable interest.

The colouring matters are found in all the organs of plants. In the madder, turmeric, and alkanet they are obtained from the roots; in logwood, Brazil wood, and fustic, they are found in the wood; in quercitron in the bark; in safflower they are furnished by the petals, and in saffron by the anthers of the flowers; whilst in the Persian berry and in annatto they are obtained from the seed.

Many colouring matters in the form in which they exist in the growing plant give little or no indication of their tinctorial power. This is the case with indigo, and with the blue colouring matters of the lichens; but by the action of fermentation and of atmospheric oxygen, or by the effect of ammonia, or by the action of other chemical agents, they may be made to furnish dye-stuffs of great brilliancy and beauty.

Most of the organic colouring matters fade or change their hue under the combined influence of oxygen and solar light; they undergo a species of slow combustion, and are in many cases rendered colourless. Many of them are also deprived of colour by reducing agents, such as sulphuretted hydrogen, the sulphides of the alkaline metals, and the salts of the protoxides of iron and of tin; but in these cases the colouring matter recovers its original hue, when it is again exposed to the air. The roots of the plant appear to exert a reducing effect upon many colouring matters, whilst in the flower the opposite effect takes place; this is beautifully shown in an experiment by Persoz:—if the roots of a transparent plant, such as balsam (*impatiens*), be immersed in a coloured solution, such as one of logwood, the coloured liquid is absorbed by the radicles, it is deprived of a portion of oxygen, and loses its colour; in this form it continues to circulate through the plant until it reaches the petals of the flowers, where it again absorbs oxygen and resumes its original hue.

All organic colouring matters are destroyed by chlorine, which acts in some cases by displacing hydrogen, in others, by decomposing water and setting oxygen at liberty, and thus producing new compounds destitute of colour. Sulphurous acid also in many instances combines with the colouring body, and produces new compounds not possessed of tinctorial power.

Almost all the colouring matters require a preparation more or less elaborate before they are fit for use; many of the processes employed in brightening and fixing their tints are of a complex nature, and still retain their original empirical character. In many of the colouring matters of organic origin, nitrogen is an essential constituent, though in a still greater number it is absent. The colouring matters in most frequent use exhibit the properties of very feeble acids. Most of them are consequently more soluble in alkaline liquids than in pure water, and they form definite insoluble compounds with the earths, and with some metallic oxides, such as those of lead and of tin. Such compounds with the metallic oxides usually possess great tinctorial or colouring power, and are termed *lakes*. The formation of these insoluble compounds is a circumstance of fundamental importance to the dyer and calico-printer, since upon it depends the general method of *mordanting*, used in the arts of dyeing and calico-printing.

(1271) Yellow Dyes.—The most important yellow dye-stuffs are quercitron, fustic, saffron, turmeric, annatto, and weld. The colouring matters of the Persian berries, of purree, and of rhubarb, are less frequently employed.

1. *Quercitron* is the bark of the *Quercus tinctoria*. It yields a yellow crystallizable principle, *quercitrin* (1266), of feebly acid properties, soluble in alcohol, sparingly so in water, freely so in alkalies.

2. The *Morus tinctoria* or *Old fustic*, is particularly employed for dyeing woollens yellow; it is also used to impart to them green and olive hues when mixed with indigo and salts of iron. Fustic furnishes a yellow colouring matter, which may be obtained in crystals by evaporating its aqueous infusion. This substance has been termed *moritannic acid* (1120) ($C_{36}H_{16}O_{20}$). It has a bitter taste, is soluble in ether, and gives a green precipitate with salts of iron. Acids and alkalies deepen the tint of the aqueous solution without producing any precipitate. When mixed with alum it produces no precipitate, but on the addition of carbonate of potash to this solution, a yellow lake is formed.

3. The *Rhus cotinus* or *Young fustic*, contains a different yellow dye, which is very soluble in water; potash renders it purple, passing into a reddish yellow; while the acetates of lead and of copper produce an orange-coloured lake with a decoction of this wood. Wool mordanted with alum acquires a bright yellow dye in a bath of this colouring principle.

4. The *Crocus sativus* yields *Saffron*, a colouring matter contained in the anthers of the flower; it is very soluble in water and in alcohol. It has been but imperfectly examined.

5. *Curcumin*, or the colouring matter of *Turmeric* (*Curcuma*

longa), is of a resinous nature; it is nearly insoluble in water, but is dissolved freely by alcohol and by ether. Alkaline solutions take it up abundantly, and change the colour to brown. This change of colour is often employed in the laboratory to indicate the presence of free alkali, since paper tinged yellow with tincture of turmeric becomes brown when immersed in a solution containing uncombined alkali. Curcumin is soluble without change of tint in the acetic, phosphoric, hydrochloric, and sulphuric acids. It is employed for dyeing wool and silk, as well as for colouring the *curry powder* of India.

6. *Annatto.*—This colouring matter is in the form of a paste, prepared from the seeds of the *Bixa orellana*, and is used for dyeing nankeen. It appears to contain an orange-red colouring substance, called *bixin*, and a yellow termed *orellin*. Bixin is a resinous matter sparingly soluble in water, but freely so in alcohol and in ether. The alkalies dissolve it, producing a deep red colour, and on neutralizing the solution with an acid it falls as an orange precipitate. The fixed oils also dissolve this colouring principle, which closely resembles that of the turmeric.

7. The root of the common *Rhubarb* yields a yellow colouring matter, termed *rhein* or *chrysophanic acid* ($C_{20}H_8O_6$?), which is also found in one of the lichens (*Parmelia parietina*). It is sparingly soluble in water, but freely soluble in the alkalies, producing a reddish brown coloured liquid, from which on the addition of acetic acid it may be precipitated in flocculi; this change from yellow to red is effected by a minute trace of alkali, so that paper stained with rhubarb may be used as a test for the presence of a free alkali. Rhein is accompanied by a portion of resin, which may be precipitated by the addition of ether to the alcoholic solution. Chrysophanic acid is soluble in ether and in hot alcohol, from which it may be obtained in crystals of a golden yellow metallic lustre.

8. The *Weld* or *Reseda luteola* also furnishes a yellow colouring matter, which is highly prized for its solidity and durability. *Luteolin*, as this substance is termed, may be extracted from the dried plant by means of boiling water; it is freely soluble in alcohol and ether, but sparingly so in water. It may be sublimed unaltered and condenses in yellow needles. Its solutions yield yellow lakes with alum, protochloride of tin, and acetate of lead.

9. *Persian Berries.*—The fruit of various species of *Rhamnus*, when gathered before it is fully ripe, contains a considerable amount of a yellow colouring matter, termed *chryso-rhamnin* ($C_{23}H_{11}O_{11}$?). This substance may be extracted by means of ether, which deposits it in brilliant stellate groups of golden yellow

crystals; an alcoholic solution of this compound yields with an alcoholic solution of acetate of lead a yellow lake (2 PbO, $C_{23}H_{11}O_{11}$?). Chryso-rhamnin is nearly insoluble in cold water, but if boiled with water it is partially dissolved, and is converted into a compound termed *xantho-rhamnin* ($C_{23}H_{12}O_{14}$?), which is also one of the constituents of the ripe berries (Kane).

10. *Purree,* or *Indian Yellow.*—This substance has been particularly examined by Stenhouse and by Erdmann. It is a colouring matter highly esteemed by artists, and is supposed to be of animal origin; it is sold in masses of three or four ounces in weight, which have exteriorly a dark brown colour, but when broken are of a bright orange-yellow. Its odour is peculiar, and resembles that of castoreum. This substance consists chiefly of the magnesian salt of a peculiar acid, termed *purreic* or *euxanthic acid.* Purree is scarcely soluble in water or in alcohol, but it is entirely soluble in boiling dilute hydrochloric, or in acetic acid; as it cools pale yellow needles of euxanthic acid (HO, $C_{42}H_{17}O_{21}$; Laurent) are deposited in stellate groups. It is somewhat soluble in boiling water, and is readily dissolved by boiling alcohol and by ether. Cold water dissolves but very little of it; alkaline solutions dissolve it, and form a yellow liquid. A solution of euxanthate of potash when mixed with the solutions of the salts of the earths gives brilliant yellow sparingly soluble precipitates; with acetate of lead it forms a yellow insoluble lake.

When euxanthic acid is heated in a small tube to a temperature a little above 212°, it melts, and a yellow sublimate of *purrenone* or *euxanthone* ($C_{40}H_{12}O_{12}$) is formed, whilst water and carbonic acid are evolved: it is also obtained by transmitting chlorine through a hot solution of euxanthic acid in absolute alcohol; and the same compound is produced when euxanthic acid is dissolved in oil of vitriol, the solution gradually depositing crystals of euxanthone. The sulphuric solution contains a new colligated acid, termed *sulphohamathionic acid,* the composition of which is doubtful.

The yellow dyes are not often used alone. They are generally employed in combination with other colours to modify shades, or to produce compound colours, as when mixed with blues to produce green.

(1272) THE RED DYES are of greater importance; of these, madder, logwood, Brazil wood, camwood, sandal wood, safflower, cochineal, and lac dye, are those in most extensive use.

(1273) 1. MADDER is the root of the *Rubia tinctorum,* a plant which is grown largely in the Levant, in the South of France, and in Alsace. It is consumed in enormous quantities for dyeing reds and purples; Turkey red cloth owes its brilliant hue to the colouring matter of this root. The composition of the madder root has been the subject of many chemical investigations, the most recent and complete being those of Rochleder and of Schunck.

According to the microscopic observations of Decaisne, the madder root, whilst growing, does not contain any red colouring matter; but its cells are filled with a yellow substance which increases in quantity with the age of the root; and this body by exposure to the air absorbs oxygen, after which the red colour is developed; an observation which agrees with the experiments of Higgin and of Schunck.

According to the last-named chemist, the madder root of commerce in addition to ligneous fibre, contains several distinct substances; viz., a bitter principle, *rubian*, which by its decomposition yields two colouring matters *alizarin* and *rubiacin*, two resins, pectic acid, and a brown substance which is probably a product of oxidation of some of the foregoing bodies. It also contains oxalate and phosphate of lime, besides other saline matters.

Some of these bodies are injurious to the brilliancy of the dye. Alizarin, according to Schunck, is the only true dyeing principle of the madder root. It has already been stated that alizarin does not exist ready formed in the growing root, but that it is produced by the decomposition of rubian; and it is well known to the dyer that the full colouring power of the root is not developed until after the dye-stuff has undergone partial fermentation.

In order to extract the whole of the colouring material, Schunck dissolves out the soluble matter from the root with water, and decomposes this solution by boiling it with dilute acid, when the whole of the colour giving portion, including the alizarin, is precipitated. If this precipitate be boiled with water, the alizarin is dissolved, and the rubiacin and the resins are left. Another plan of obtaining alizarin consists in reducing the root to a coarse powder, treating it with hot sulphuric acid, and well washing it till the last traces of acid are removed; the earthy matters are thus rendered soluble, and everything which water will take up is removed; but nearly the whole of the alizarin remains untouched, since it is insoluble in water containing free acid; the undissolved mass when dried is largely used in the print works under the name of *garancin.* By boiling this garancin in a large quantity of water, the colouring matter is dissolved and on adding sulphuric acid it is precipitated mixed with several impurities. If this precipitate be well washed, dried, and submitted to sublimation, beautiful orange-coloured needles of alizarin are obtained; these, if washed with cold alcohol and dried, are perfectly pure.

(1274) *Alizarin* ($C_{14}H_5O_4$, 3 Aq, Schunck; $C_{20}H_6O_6$, 4 Aq, Strecker).—This is a red crystalline matter destitute of odour and of taste; it is neutral to test papers, and is almost insoluble in cold water. It is but sparingly soluble in hot water; hot alcohol dissolves it more freely, and if this solution be evaporated, alizarin is deposited in plates resembling those of mosaic gold. It is also soluble in ether; acids brighten its tint but do not dissolve it. Potash dissolves it freely, and strikes a beautiful purple, but it is precipitated unaltered on adding an acid; with lime, baryta, and oxide of iron, it forms insoluble purple lakes. With alumina it forms a beautiful red lake. Alizarin is not decomposed even by boiling sulphuric acid, which dissolves it, and on dilution deposits it unchanged. Boiling dilute nitric acid converts alizarin into phthalic (alizaric) acid, and probably into oxalic acid (Strecker and Wolff), whilst nitrous vapours are evolved:—

$$\overbrace{C_{20}H_6O_6}^{\text{Alizarin.}} + 2\,HO + 8\,O = \overbrace{2\,HO, C_{16}H_4O_6}^{\text{Phthalic Acid.}} + \overbrace{2\,HO, C_4O_6}^{\text{Oxalic Acid.}}.$$

The crystals of alizarin deposited from its spirituous or aqueous solution lose about 18 per cent. of water at 212°. By a heat of about 420° alizarin is sublimed, but part of it undergoes decomposition. The sublimate forms beautiful, transparent, orange-coloured needles, which are anhydrous and of high lustre.

(1275) *Rubian* ($C_{56}H_{34}O_{30}$? Schunck); the *Ruberythric Acid* of Rochleder?—This is a bitter uncrystallizable principle, which under the influence of acids, of alkalies, and of a peculiar azotized ferment (*Erythrozym*) contained in the madder root, is broken up into a fermentable sugar, and into alizarin and other colouring matters. Synaptase produces a similar decomposition of rubian.

The preparation of rubian in a state of purity is not easy. Schunck takes advantage of its tendency to contract a superficial combination with charcoal, and recommends that ground madder be digested in hot water, (1 lb. of madder to a gallon of water); that the undissolved portion be strained off, and that to each gallon of the hot liquid an ounce of bone charcoal be added. The mixture after brisk agitation is to be allowed to settle, and the charcoal collected on a filter and washed with cold water, until the washings no longer become green when heated with hydrochloric acid. The charcoal while in this condition is saturated with rubian; it is next to be boiled with alcohol, and this treatment is to be repeated so long as fresh alcohol acquires a yellow colour when boiled with the charcoal. The alcoholic solutions on evaporation yield rubian, contaminated with a variable amount of lime, and with a green colouring matter: this colouring matter may, however, be got rid of by treating a solution of the rubian in water a second time with charcoal, and repeating the entire process. The alcoholic solution when evaporated leaves the rubian in the form of a brittle transparent mass of a dark yellow colour, resembling dried gum or varnish.[*] It is not deliquescent, but is abundantly soluble in water, less freely so in alcohol, and insoluble in ether. When heated to about 266° it melts, swells up, disengages water, and gives off orange vapours of alizarin, leaving a bulky carbonaceous residue.

Solutions of rubian are of a pale yellow colour; they are not precipitated by the metallic salts generally, but if mixed with subacetate of lead an insoluble compound is formed. Alkalies change the colour of a solution of rubian into blood red, but, if they be afterwards neutralized by the addition of an acid, the yellow tint is restored: if, however, the alkaline liquid be boiled, its colour changes to purple, and on the addition of an acid red flocculi are precipitated. Oil of vitriol forms a blood-red solution with rubian. Cold nitric acid has little action upon rubian, but when heated with it, red nitrous fumes are evolved, and *alizaric* (phthalic) acid (1331) is found in the liquid.

If a solution of rubian be boiled with dilute sulphuric or hydrochloric acid, orange-coloured flocculi are precipitated, and an uncrystallizable sugar remains in the liquid. These coloured flocculi consist of alizarin, rubianin, and two resins. For the mode of separating these bodies the reader is referred to Schunck's paper (*Phil. Trans.* 1851, p. 445).

Rubianin ($C_{44}H_{24}O_{20}$?) is deposited from its solution in boiling alcohol in silky lemon-yellow crystals, which are soluble in boiling water. Oil of vitriol dissolves it with a yellow colour; on the application of heat to this solution it becomes blackened, and evolves sulphurous acid. Nitric acid dissolves but does not decompose it.

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[*] Rochleder's ruberythric acid was obtained in crystals from an infusion of madder by separating the alizarin and other colouring matters by means of neutral acetate of lead, and then precipitating the rubian with subacetate of lead, decomposing this precipitate with sulphuretted hydrogen, and boiling the sulphide of lead with alcohol (the rubian accompanies the sulphide of lead). The rubian is dissolved by the alcohol, and is to be combined with baryta, dissolved in dilute acetic acid, re-precipitated by subacetate of lead, and again treated with sulphuretted hydrogen after the lead precipitate has been diffused through alcohol. On evaporation of the alcoholic solution ruberythric acid is left in crystals ($C_{72}H_{40}O_{14}$?). Schunck considers this body to be the result of the decomposition of rubian, and not rubian itself.

Rubiacin ($C_{32}H_{11}O_{10}$? Schunck) is one of the components of commercial madder; it assumes the form of beautiful orange coloured tables, or of brilliant yellow needles, resembling those of iodide of lead. It is sparingly soluble in boiling water, but is readily dissolved by alcohol; it may with ease be sublimed unaltered. Rubiacin is a compound of considerable stability; its solution in oil of vitriol may be boiled without undergoing decomposition. Hydrate of alumina acquires an orange tint when digested with an alcoholic solution of rubiacin.

When rubiacin is dissolved in a solution of perchloride or pernitrate of iron it gives a brownish red liquid, which on the addition of an acid deposits flocculi of *rubiacic acid* ($HO, C_{32}H_8O_{16}$?). This body is dissolved by the alkalies with a purple colour.

For further details, the reader is referred to the papers of Schunck, Liebig's *Annal.* lxvi. 175: *Phil. Trans.* 1851, 1853, 1855; and of Rochleder, Liebig's *Annal.* lxxx. 321, lxxxii. 205.

(1276) 2. Logwood.—This valuable dye-stuff is extensively employed for dyeing black with alum, but acids change the colour to red. It is the produce of the *Hæmatoxylon Campechianum.* It contains a crystalline matter termed *hæmatoxylin* ($C_{32}H_{14}O_{12}$, 2 Aq. and 6 Aq.; Gerhardt), which, however, in its pure state is not red, but straw-yellow or honey-yellow. Under the influence of the alkalies and of oxygen it assumes an intensely red colour. In order to extract hæmatoxylin, powdered logwood mixed with quartzose sand (to prevent it from agglomerating into masses) is digested for several days with five or six times its volume of ether. The liquid is distilled until it acquires the consistence of syrup; it is then to be mixed with water, and set aside in a vessel loosely covered. In the course of a few days the hæmatoxylin is deposited in crystals. Logwood thus treated yields from one-eighth to one-tenth of its weight of this substance.

The crystals of hæmatoxylin are transparent, and consist of long, yellow, brilliant four-sided needles: these crystals contain six equivalents of water, which they lose at 212°. If a solution of hæmatoxylin saturated at the boiling point be allowed to cool in a closed vessel, granular crystals with 2 Aq. are deposited. Hæmatoxylin has a sweet taste, free from astringency, like that of liquorice. It is sparingly soluble in cold water, but freely so in boiling water. Ether and alcohol dissolve it freely.

Solution of acetate of lead gives in one of hæmatoxylin a white precipitate, which speedily becomes blue; salts of copper give a dirty green precipitate, which also quickly becomes blue; chloride of barium occasions a red precipitate; protochloride of tin gives a rose-coloured lake, and iron alum a scanty blackish violet precipitate; ordinary alum gives a red solution, but does not occasion any precipitate.

Sulphuric and hydrochloric acids have but little effect upon hæmatoxylin, but dilute nitric acid colours it red. Concentrated nitric acid converts it into oxalic acid.

Solution of potash communicates a violet tint to one of hæmatoxylin, and if the air have access to the solution, it becomes first blue and then brown, whilst oxygen is absorbed. Solutions of hæmatoxylin are not altered by exposure to the air, but if ammonia be present oxygen is absorbed, and a purple liquid is formed, which contains hæmateate of ammonia:—

$$\overbrace{C_{32}H_{14}O_{12}}^{\text{Hæmatoxylin.}} + O_2 + 2\,H_3N = 2\,HO + \overbrace{2\,H_3N, C_{32}H_{12}O_{12}}^{\text{Hæmateate of Ammonia.}}.$$

The ammonia may be removed from this compound by means of acetic acid, when the *hæmatein* ($C_{32}H_{12}O_{12}$) is precipitated in voluminous red flocculi, resembling hydrated peroxide of iron. Hæmatein is sparingly soluble in cold water, but is more readily soluble in boiling water, and the solution on evaporation yields a confused mass of green crystals with a metallic lustre. Sulphuretted hydrogen deprives hæmatein of its colour, but does not reconvert it into hæmatoxylin (Gerhardt).

Potash dissolves hæmatein with a blue colour, which becomes brown when exposed to the air. Its ammoniacal solution is of a fine purple, which also becomes brown on exposure. Hæmateate of ammonia yields coloured precipitates with many metallic salts; with acetate of lead it gives a deep blue, with sulphate of copper a violet blue, with protochloride of tin a violet, and with iron alum a black precipitate.

(1277) 3. Brazil-wood is the produce of the *Cæsalpinia Braziliensis*. It yields by treatment with alcohol yellow or orange crystals of *brezilin*, which are likewise soluble in water and ether. Acids, especially the citric, give it a bright yellow colour; with alkalies it gives a violet or purple colour: hence it is sometimes used as a test of their presence in a free state. Brezilin forms, in combination with alumina, the basis of *red ink*. Like hæmatoxylin, it is bleached by nascent hydrogen and by sulphuretted hydrogen. *Sapan-wood* and *camwood* are stated to yield the same colouring principle as Brazil wood.

Sandal wood, alkanet root, and some other substances also afford red dyes, but in general the vegetable red colours are fugitive. The colouring matter of alkanet is soluble in oils.

(1278) 4. SAFFLOWER is obtained from the petals of the *Carthamus tinctorius.* These petals contain two colouring principles, one of which is yellow and soluble in water, but is of no value to the dyer: it is a weak acid, of a bitter taste. If an infusion of safflower be mixed with an acetic solution of acetate of lead, a soluble yellow salt of lead is formed, which on the addition of ammonia is precipitated in dark yellow flocculi.

The really valuable colouring principle of the safflower is red, and is employed for artists for *pink saucers,* and for imparting a beautiful and brilliant rose-red to silk; but it fades quickly when exposed to the sun's light.

Carthamin ($C_{28}H_{16}O_{14}$), as this substance is termed, is insoluble in water and in acids, but is easily dissolved by the alkalies; on adding an acid to the solution it is again precipitated: it is also soluble in alcohol. Carthamin may be obtained by digesting safflower in weak acetic acid, in order to remove the yellow dye-stuff; the washed dye is next digested in a solution of carbonate of soda; a skein of cotton is then placed in the liquid, and lemon-juice, or a solution of citric acid, is added. The cotton yarn mechanically removes the flocculent precipitate of carthamin from the liquid; the yarn must be washed with cold water, the colouring matter again dissolved by carbonate of soda, and reprecipitated by the addition of citric acid. Carthamin when dry is a red pulverulent substance; it has a greenish metallic lustre when viewed in mass, but in thin layers it is of a beautiful purplish red. Its solutions in alkalies gradually absorb oxygen and become altered.

(1279) 5. CARMINE is contained in the *Coccus cacti,* being the colouring matter of the cochineal. After treating the powdered insects with ether to remove the fat, the insoluble portion is digested in water, and, on adding acetate of lead, a lead lake is precipitated of a purple colour. This must be well washed, decomposed by sulphuretted hydrogen, and the filtered solution evaporated to dryness *in vacuo* over sulphuric acid. De la Rue finds the colouring matter of the cochineal thus obtained to be an acid body, which he terms *carminic acid* ($C_{28}H_{14}O_{16}$). It is a purple brown, friable mass, soluble in all proportions in alcohol and in water, but very slightly soluble in ether; it may be dissolved unchanged in strong [illegible] and hydrochloric acids. Nitric acid even if dilute decomposes it; chlorine, iodine, and bromine, also decompose it, and change its colour to yellow. The fixed alkalies change the colour of the aqueous solution to purple: the alkaline earths give purple precipitates; with alum no lake is produced till ammonia is added, when it falls as a beautiful crimson precipitate. The lakes, with acetate of lead, and with salts of copper, zinc, and silver, are purple; with salts of tin a bright crimson solution is obtained.

When carminic acid is treated with dilute nitric acid it yields an acid of a yellow colour, which crystallizes in rhombic plates; it is very soluble in boiling water, in alcohol, and in ether. It is termed *nitrococcussic acid* ($2\ HO, C_{16}H_3(NO_4)_3O, 2\ Aq$), and is isomeric with trinitranisic acid. It deflagrates strongly when heated. Its salts are soluble in water, and most of them are also dissolved by alcohol. Cochineal is extensively employed, in combination with oxide of tin, as a scarlet dye for cloth.

6. LAC DYE is very similar to cochineal in its nature, being also furnished by a species of coccus. Of late years this dye-stuff has been extensively substituted for the more costly cochineal, and it furnishes scarlets equally vivid, and even more permanent, but the pinks are not so good. In dyeing scarlets the liquid employed for dissolving the colouring matter is a solution of tin in concentrated hydrochloric acid, 20 lb. of acid being required for each pound of tin; the dye-stuff is digested in an equal weight of this liquid, and the cloth, after being cleansed by boiling with fuller's earth, is introduced into a bath containing a *mordant* composed of a solution of protochloride of tin, prepared by gradually dissolving 4 lb. of tin in a mixture of 27 lb. of hydrochloric acid, and 1½ lb. of nitric acid (sp. gr. 1·19). In order to dye 100 lb. of cloth, the following process, according to Ure, is adopted:—300 gallons of water are raised to 150° in a tin boiler, and 1½ lb. of solution of tin mordant and a handful of bran are added; when the liquor boils it is skimmed, and 10½ lb. of lac dye previously dissolved in the acid, and 23½ lb. of mordant, are introduced; immediately after which 10½ lb. of bitartrate of potash, and 4 lb. of ground sumach are suspended in a bag in the bath for five minutes, and then withdrawn; the fire is now extinguished, and 20 gallons of cold water containing 10 lb. of tin mordant are added, after which the cloth is introduced; the liquid is then boiled for an hour, and at the end of that time the cloth is withdrawn and well rinsed.

(1280) 7. EXTRACT OF ALOES.—This substance may, by the action of nitric acid, be made to yield various compounds, which admit of being fixed by means of mordants upon silken and woollen fabrics, to which they impart dyes of great durability and beauty. Extract of aloes contains a compound which is soluble both in water and in alcohol, termed *aloin;* when exposed to the air it absorbs oxygen, and becomes of an intense red colour.

Aloin ($C_{34}H_{18}O_{14}$? Stenhouse).—In order to extract this substance, powdered Barbadoes aloes, mixed with sand to prevent the particles from agglomerating, are treated with cold water; the dark liquid thus obtained, if evaporated *in vacuo* to the consistence of syrup, and left for a few days in a cool place, deposits granular crystals, which are more or less deeply coloured: these must be pressed between folds of blotting paper, and recrystallized from water, the temperature of which is not to exceed 150°. Aloin may also be obtained in crystals from a warm alcoholic solution, in groups of pale yellow needles. Cape aloes and Socotrine aloes also contain aloin, but it is accompanied by a large proportion of foreign matters, which interfere with its crystallization. Aloin is a neutral substance, with a sweetish, intensely bitter, persistent taste. It constitutes the purgative ingredient in aloes. At a temperature of 212° it is rapidly altered; at 300° it melts, and if heated strongly in the open air it burns with a smoky flame. The alkalies, both caustic and carbonated, dissolve it readily, forming orange-coloured solutions.

When extract of aloes is treated with nitric acid it yields *Chrysammic acid* ($HO, C_{14}H(NO_4)_2O_3$?). This compound is obtained by treating extract of aloes for some days with 8 times its weight of nitric acid (sp. gr. 1·37), distilling off the greater part of the acid, and then adding water; chrysammic acid is precipitated. It is nearly insoluble in water, but soluble in alcohol and in ether, from which it may be obtained in golden yellow plates; on the application of heat it is decomposed with explosion. Its salts are soluble in hot water and form deep red solutions; most of them may be crystallized, and the crystals exhibit a metallic lustre. Ammonia dissolves the acid with the formation of a beautiful purple-coloured solution, from which, on the addition of a neutral salt, such as nitrate of potash, an amidated compound is deposited in brilliant dark green needles, which exert a polarizing action upon light which is transmitted through them.

Schunck finds other acids in the mother liquor from which the chrysammic acid has been separated; one of these, termed *chrysolepic acid*, appears to be identical with carbazotic acid; two other resinoid acids, the *aloetic* ($HO, C_{14}H_2(NO_4)_2O$, Aq ?), and *aloeretinic*, are also formed at the same time; they have an intensely bitter taste, and form red salts.

(1281) **Blue Dyes.—1. Indigo.**—The most important of the blue colouring matters, and the one which has been most accurately studied, is indigo, which is chiefly obtained from the leaves of various species of the *Indigofera*. Crude indigo contains a definite colouring material, termed *indigotin*, or indigo blue, from which numerous derivatives belonging to the indigo series have been obtained. Such of them as contain nitrogen have hitherto been procured from natural indigo only, but by the metamorphosis of these azotized compounds, bodies of a less complicated order have been obtained, many of which belong to the salicylic, the kinic, and the phenic groups. The following are the most important of the immediate derivatives of indigo: if indigo blue be described under the term *indyl*, their relations to it will then be represented by the formulæ of the fourth column:—

Indigo-blue . . .	$C_{16}H_5NO_2$	=	Indyl	In
White Indigo . .	$C_{16}H_6NO_2$	=	Hydride of Indyl	In, H
Isatin	$C_{16}H_5NO_4$	=	Oxide of Indyl	In, O_2
Isatic acid .	$HO, C_{16}H_6NO_5$	=		HO, InO_3
Isathyd	$C_{16}H_6NO_4$	=	Oxide of Indyl and of hydrogen	$\left.\begin{array}{l}\mathrm{In}\\ \mathrm{H}\end{array}\right\} O_2$
Indin	$C_{32}H_{10}N_2O_4$	=	Polymeride of Indyl	In_2
Hydrindin . . .	$C_{32}H_{11}N_2O_4$	=	Hydride of Indin	In_2, H.

(1282) *Condition of Indigo in the Plant.*—Indigo is extracted from the leaves of a variety of plants, principally the produce of India and America: it is especially obtained from the various kinds of *Indigofera*. The produce of the *Indigofera anil* was particularly examined by Chevreul: the *Isatis tinctoria*, or common woad, and several other plants, also yield indigo in small quantity, and it has been stated to occur occasionally in the milk of cows, and in human urine; so that indigo may be produced under circumstances apparently widely different.

The blue colouring matter of indigo is not soluble in water or in alkaline leys, but by treatment with deoxidizing agents, in contact with water, it may be made to combine with an additional equivalent of hydrogen, and produce a white substance, termed *reduced indigo*, which is also insoluble in water, but is soluble in alkaline leys. When an alkaline solution of this reduced indigo is exposed to the air it absorbs oxygen, and is converted into indigo blue, which is precipitated in the insoluble form.

it is to avoid the use of boiling water in the preparation of indigo on the large scale. Solutions of indican which have been mixed with alkalies, and then boiled with acids, yield no indigo blue, but a mixture of this humus-like body and resin.

Extraction of Indigo.—If the dried leaves of the *Indigofera* be digested in cold water for some hours, a green solution is obtained, which when exposed to the air undergoes fermentation, during which indigo is separated in the form of a blue sediment. The mode of preparing indigo, usually adopted in the East Indies, is stated to be the following:—the green plants, cut at the flowering time, are placed in wooden troughs and covered with water; after the lapse of a few hours a sort of fermentation takes place in the mixture, ammonia and carbonic acid are disengaged, and the liquid in the troughs becomes covered with a blue iridescent film. The liquid is at this stage drawn off into other troughs, where a small quantity of lime is added, and, on briskly agitating the mixture, the pigment separates as a deep blue granular powder. This is drained on calico, pressed, cut into cakes, and dried.

The indigo of commerce is by no means a homogeneous body. Its most important constituent is *indigotin*, or indigo blue, but it contains several other substances, and in particular two bodies, known as *indigo brown* and *indigo red*. The brown colouring matter is soluble in potash: the indigo red may be extracted by means of boiling alcohol.

(1283) *Indigo blue* or *Indigotin* ($C_{16}H_5NO_2$) may be separated from these impurities by the process of sublimation. If a small quantity of indigo be heated between two watch-glasses so as to protect it from the air, a considerable proportion of it is decomposed, but a portion becomes condensed in light copper-coloured six-sided crystals upon the surface of the mass operated on. Pure indigo blue is, however, obtained more abundantly by the following plan:—4 ounces of commercial indigo in fine powder, and 4 ounces of grape sugar, are placed in a flask capable of containing 10 pints of liquid; 6 ounces of a saturated solution of caustic soda are then added, and the flask is filled up with boiling alcohol; it is then closed so as to prevent the access of air, and the mixture after agitation is set aside. In a few hours it becomes clear; the yellowish red solution is then drawn off with a syphon, and if left exposed in open vessels it rapidly absorbs oxygen, becomes brown, and deposits crystals, which after being treated first with alcohol, and then with hot water, and dried, form perfectly pure indigo blue. Good indigo yields nearly half its weight of crystallized indigo blue (Fritsche).

Indigotin fuses at about 550°, and furnishes purple vapours. Amongst the products of its destructive distillation are hydrocyanate and carbonate of ammonia, aniline, and a peculiar empyreumatic oil. Indigo blue is metameric with cyanide of benzoyl. It is insoluble in water, alcohol, ether, the fixed and volatile oils, as well as in dilute acids and alkalies.

(1284) *Compounds of Indigo with Sulphuric Acid.*—Sulphuric acid appears to form several compounds with indigo; two of them have been analysed, viz., the *sulphindylic*, or *sulphindigotic* acid, and the *sulphopurpuric*, or *sulphophenicic acid*; a third acid, the *hyposulphindigotic*, appears also to be produced along with the foregoing acids.

Sulphindylic Acid ($HO, C_{16}H_4NO, S_2O_6$).—When commercial indigo is triturated with 6 times its weight of fuming sulphuric acid, considerable heat is developed, and a blue solution is formed, which is extensively used for dyeing cloth, under the name of *Saxony blue*. Ordinary oil of vitriol may also be employed to dissolve indigo, but more than double the quantity of such acid is required, and it must be heated to 130° or 140°. If a sufficient amount of acid be employed, almost the whole of the indigo may be dissolved, and if the liquid be allowed to stand for a few hours, it will remain clear on being diluted. The filtered liquid contains a mixture of sulphindylic and hyposulphindigotic acids. If the original acid liquid be diluted with from thirty to fifty times its bulk of water, and flannel which has been washed with soap and carbonate of soda, and then with water, be immersed in the liquid, the indigo acids will attach themselves to the flannel, leaving the excess of sulphuric acid in the mother liquor. The colouring matter may be entirely removed from the flannel by digesting it in a dilute solution of carbonate of ammonia: a deep blue liquid is thus obtained, which, when evaporated to dryness and treated with alcohol, is separated into sulphindylate of ammonia, which is insoluble, and hyposulphindigotate of ammonia, which is dissolved by the alcohol.

Sulphindylate of potash ($KO, C_{16}H_4NO, S_2O_6$) is sparingly soluble in cold water, and is precipitated in flocculi, when acetate of potash is added to a crude solution of indigo in sulphuric acid, after dilution with 10 parts of water. The sulphindylates form blue solutions, which appear red when held between the eye and the sun. These solutions are rendered colourless by the action of reducing agents, but regain their blue colour by exposure to the air.

Sulphopurpuric Acid ($2\,C_{16}H_5NO_2,\ S_2O_6 = HO,\ C_{32}H_9N_2O_3,\ S_2O_6$).—This constitutes the greater part of the insoluble residue which is left upon the filter when indigo is treated with a proportion of sulphuric acid too small to dissolve it wholly. It is insoluble in liquids containing free acid; but it forms a blue solution in pure water. When acetate of potash is added to this liquid it gives a purple precipitate of sulphopurpurate of potash.

(1285) ***Reduced Indigo, White Indigo,*** or ***Indigogen*** ($C_{16}H_6NO_2$). When blue indigo is treated with deoxidizing agents, such as a mixture of protosulphate of iron and potash, a yellow solution is formed, containing ***reduced*** indigo, a compound in which 1 equivalent more of hydrogen is present than in blue indigo. On neutralizing the alkaline liquid by acetic acid, the reduced indigo falls in dirty white flocculi, which are insoluble in water, but slightly soluble in alcohol and in ether; even when dry they gradually absorb oxygen from the air, but the absorption is much more rapid when moist, water and indigo blue being reproduced. The dilute acids are without effect upon reduced indigo; but fuming sulphuric acid dissolves it, forming a deep purple liquid; if diluted with water it becomes blue, and is converted into sulphindylic acid. The alkaline solutions of reduced indigo are precipitated by many of the solutions of the metals, and the compounds thus formed speedily become blue by exposure to the air.

The reduction of indigo from the blue to the white form may be effected by several processes:—

1. By means of sugar, on Fritsche's plan, which has been already described (1283).

2. By the action of a mixture of protosulphate of iron and some alkali. Advantage is taken of this in the preparation of the indigo bath for dyeing purposes. The ***copperas vat,*** as it is termed, is employed in dyeing cottons and linen goods. The proportions to be used will vary with the quality of the indigo, but for laboratory purposes the following ingredients may be employed:—1 part of powdered indigo, 2 of sulphate of iron, 3 of slaked lime, and 150 or 200 of water. The reaction is somewhat complicated; the lime acting on the sulphate of iron sets free hydrated protoxide of iron, and this oxide in the presence of water takes up an additional quantity of oxygen, becoming converted into the hydrated peroxide, whilst the liberated hydrogen unites

with the indigo blue, and constitutes reduced indigo, which becomes dissolved by the excess of lime, forming a yellow solution:—

$$2\,(FeO, SO_3) + 2\,(CaO, HO) = 2\,(FeO, HO) + 2\,(CaO, SO_3)\text{; and}$$

$$2\,(FeO, HO) + HO + \overbrace{C_{16}H_5NO_2}^{\text{Indigo Blue.}} = Fe_2O_3,\ 2\,HO + \overbrace{C_{16}H_6NO_2}^{\text{White Indigo.}}$$

If the alkaline liquid thus obtained be exposed to the air, it becomes covered with a blue film, and deposits nearly pure indigo, and if mixed with hydrochloric acid, in vessels filled with carbonic acid, white indigo is obtained. If yarn or woven goods be immersed in such a solution, and then exposed to the air, the reduced indigo rapidly absorbs oxygen, and becomes converted into blue indigo within the fibres of the tissue, with which it contracts an intimate adhesion. The blue dye thus obtained is very intense and permanent, since it is insoluble in all ordinary solvents.

3. By means of orpiment and protochloride of tin, which are sometimes substituted in calico printing, as reducing agents in the place of the protosulphate of iron; in this case potash is employed instead of lime water as the solvent of the reduced indigo.

4. By means of decaying vegetable matter, which answers the same purpose as the sulphate of iron. This vat is chiefly used for dyeing yarns, and is prepared by some manufacturers in the following manner:—4 parts of finely powdered indigo, 50 of woad, 2 of madder, and 2 of carbonate of potash, are mixed with 2000 of water, and the mixture is kept for some hours at a temperature of about 194°; 1⅓ part of recently slaked lime is then added in small quantities at a time, after which fermentation commences; formic, acetic, and carbonic acids are formed, as well as ammonia. The lime reduces the carbonate of potash to the caustic state, and enables it to dissolve the indigo which has been reduced during fermentation by the decomposition of the vegetable matter. The addition of the lime is attended with the further advantage of precipitating a portion of brown colouring matter that would otherwise deaden the tint of the goods. The foam or *flower* of the vat has a beautiful blue iridescent appearance caused by reoxidation of the indigo at the surface, but the liquid beneath is of a deep yellow colour; by exposure to air it becomes green and finally deposits blue indigo. To prevent this reoxidation the vats are kept covered when not in actual use; and fresh materials are added from time to time in order to maintain the liquor at a uniform strength.

Starch, sugar, bran, and other vegetable matters may be substituted for the madder and the woad in the indigo vat. These substances undergo fermentation, and act as deoxidizing agents; probably lactic and butyric acids are generated, and the indigo is reduced by the hydrogen, while the latter is in the act of being liberated.

(1286) *Assay of Indigo.*—The quality of commercial indigo varies greatly; the purest specimens usually occur in small masses of an intense violet-blue colour, which by friction with a hard smooth body acquire a coppery lustre. The best kinds are sufficiently light to float upon water, and when broken they do not contain cavities which exhibit brown or whitish veins. Indigo is, however, frequently adulterated with sand, with starch, and sometimes, it is said, with powdered lead. Good indigo should not leave more than from 5 to 8 per cent. of ash, calculated upon the dried mass; during drying it loses from 5 to 8 per cent. of water. Starch may be detected by treating the indigo with boiling water very faintly alkalized, and, after neutralizing the filtrate, testing it with iodine.

A simple method of determining the relative value of any sample of indigo, has been proposed by Bolley, who estimates its tinctorial power by measuring the amount of a standard solution of chlorate of potash, which is required to destroy the blue colour of a given sample:—10 grains of the indigo for assay are reduced to a very fine powder, and triturated with 2 fluid drachms of fuming sulphuric acid; the mixture is allowed to digest for twelve hours in a closed vessel with occasional agitation. The indigo must be completely dissolved before the next part of the process is commenced. As soon as the solution is effected, the liquid is to be poured into a capsule with about a pint of water, containing an ounce of pure hydrochloric acid, and the mixture is brought to the boiling point. A solution of chlorate of potash containing 2·5 grains of the salt in 1000 grains of water, is then to be added from an ordinary alkalimeter, drop by drop to the boiling liquid; the blue colour first becomes green, then greenish-brown, and when the last tinge of green disappears and has been replaced by a reddish-brown, the operation is complete. The number of divisions of the liquid required does not indicate the percentage of indigo blue, but simply the relative value of the different samples compared together.

Penny substitutes bichromate of potash for the chlorate; 100 parts of pure indigo blue requiring exactly 75 of the bichromate for decoloration: by this means an exact determination of the amount of indigo blue may be effected.

(1287) *Products of the Oxidation of Indigo.*—The action of oxidizing agents upon indigo gives rise to several interesting products. Concentrated chromic acid breaks up the constituent molecule of indigo, and occasions a copious disengagement of carbonic acid; but if a more dilute solution of chromic acid be employed, the indigo is converted into *isatin:* a similar change is effected by the action of dilute nitric acid:—

$$\overbrace{C_{16}H_5NO_2}^{\text{Indigo Blue.}} + O_2 = \overbrace{C_{16}H_5NO_4}^{\text{Isatin.}}.$$

The oxidizing action proceeds further if the indigo be treated with nitric acid in a more concentrated form; thus, if indigo be boiled with fuming nitric acid diluted with 10 or 12 parts of water, indigotic, or nitro-salicylic acid is formed (HO, $C_{14}H_4,NO_4,O_5$; 1233); and by a prolonged action of the nitric acid, carbazotic acid (HO, $C_{12}H_2(NO_4)_3O$; 1326) is produced; both these compounds contain less carbon than the true indigo group, and this carbon is probably separated in the form of carbonic or of oxalic acid.

The oxidizing effect of hydrate of potash upon indigo is somewhat different from that of nitric acid. If indigo in fine powder be boiled with a solution of potash (of sp. gr. 1·36), it is dissolved without the extrication of gas, and an orange-coloured liquid is formed, which on cooling deposits yellow crystals. If these crystals be dissolved in water, and treated with an excess of hydrochloric acid, a dirty bluish-red precipitate is formed; this substance constitutes Fritsche's *chrysanilic* acid, but according to Gerhardt, the precipitate consists of a mixture of reduced indigo with isatin, and the chemist last named represents the action of the solution of hydrate of potash on indigo thus:—

$$3\,\overbrace{(C_{16}H_5NO_2)}^{\text{Indigo Blue.}} + KO,HO + 2\,HO = \overbrace{KO,C_{16}H_6NO_5}^{\text{Isatate of Potash}} + 2\,\overbrace{(C_{16}H_6NO_2)}^{\text{White Indigo.}}.$$

By exposure of the solution of the yellow crystals to the air, oxygen is absorbed and indigo blue is deposited. If indigo be fused with hydrate of potash, hydrogen is evolved and salicylic acid is amongst the products; but if to a concentrated boiling solution of potash indigo be added, care being taken to replace the water as it evaporates, and if to the boiling liquid powdered peroxide of manganese be added until the solution ceases to deposit indigo when exposed to the air, a different compound is the result, and anthranilic acid is obtained in combination with potash.

Anthranilic acid ($HO, C_{14}H_6NO_3$) may be procured by neutralizing the potash with sulphuric acid, evaporating to dryness, dissolving the anthranilate of potash by means of alcohol, which leaves the sulphate, and decomposing the anthranilate of potash by the addition of acetic acid. On evaporating the alcoholic solution, this acid is obtained in brilliant plates, or in four or six-sided needles. Anthranilic is metameric with benzamic acid (1209). If heated gently it may be sublimed unchanged, but if the temperature be suddenly raised the acid becomes decomposed into aniline and carbonic acid:—

$$\overbrace{HO, C_{14}H_6NO_3}^{\text{Anthranilic Acid.}} = \overbrace{C_{12}H_7N}^{\text{Aniline.}} + 2\,CO_2.$$

(1288) *Isatin* ($C_{16}H_5NO_4$).—This substance, which contains two equivalents more of oxygen than indigo blue, may be obtained by heating indigo in a dilute solution of bichromate of potash and sulphuric acid, or by the following process:—Powdered commercial indigo, of good quality, is to be mixed with a sufficient quantity of water to reduce it to a thin cream, and the mixture is to be gently heated; nitric acid must then be added in small quantities at a time until the blue colour has disappeared; 10 parts of indigo require 6 or 7 parts of acid. The mass must next be largely diluted with water, boiled, and filtered whilst boiling hot; the undissolved residue must be again boiled with water, and the filtered solution added to the first portions: crystals are deposited as the liquid cools; they must be washed with water containing a little ammonia, then dissolved in alcohol and recrystallized.

Isatin crystallizes in brilliant orange-coloured rhombic prisms; it is sparingly soluble in cold water, but is readily dissolved by boiling water and by alcohol. On the application of heat to the crystals they melt and are volatilized, emitting acrid vapours of a yellow colour. When isatin is distilled in closed vessels a considerable portion of it undergoes decomposition. Isatin is capable of exchanging an equivalent of hydrogen for one of a metal; thus, if an alcoholic solution of isatin be mixed with one of nitrate of silver, a wine-red amorphous precipitate of *argentisatin* ($C_{16}H_4AgNO_4$) is formed. Solution of potash dissolves isatin freely, and forms a purple liquid, which on boiling becomes yellow. When examined after this change of colour has occurred, the elements of the isatin are found to have combined with those of water, thus producing *isatic acid* ($HO, C_{16}H_6NO_5$), which remains in combination with the potash.

If isatin be heated with solid hydrate of potash it is decomposed, hydrogen is liberated, carbonic acid is formed and is retained in combination with the potash, whilst aniline distils over:—

$$\overbrace{C_{16}H_5NO_4}^{\text{Isatin.}} + 4\,(HO, KO) = \overbrace{C_{12}H_7N}^{\text{Aniline.}} + 4\,(KO, CO_2) + H_2.$$

(1289) The *action of chlorine upon indigo* is peculiar; it immediately discharges the blue colour, and produces (in addition to formic acid, muriate of ammonia, and a brown resinous substance) four distinct chlorinated compounds. Two of these, viz., *chlorisatin* $C_{16}H_4ClNO_4$, and *dichlorisatin* $C_{16}H_3Cl_2NO_4$, are yellow, sparingly soluble, crystallizable substances formed upon the type of isatin. A third chlorinated compound is *trichloraniline* ($C_{12}H_4Cl_3N$), and it is usually accompanied by a certain quantity of *trichlorophenic* acid ($HO, C_{12}H_2Cl_3O$). Chlorisatin and dichlorisatin are soluble in alcohol; when heated with a solution of potash they yield acids,—the *chlorisatic* ($HO, C_{16}H_5ClNO_5$), and *dichlorisatic acid* ($HO, C_{16}H_4Cl_2NO_5$), corresponding with isatic acid; and, if distilled with hydrate of potash they give chlorinated bases of a composition corresponding to that of aniline,—

Chloraniline being composed of $C_{12}H_6Cl\,N$, and
Dichloraniline of . . . . $C_{12}H_5Cl_2N$.

The reaction is precisely analogous to that with pure isatin (see p. 41).

The action of bromine upon indigo is analogous to that of chlorine, though it is less violent.

(1290) *Ammoniacal derivatives of Isatin.*—When isatin is treated with ammonia it gives rise to a number of amidated products, the composition of which varies with the degree of concentration of the ammonia: they have been particularly studied by Laurent (*Ann. de Chimie,* III. iii. 483). The following table exhibits the reactions which attend their formation:—

$$\begin{array}{lrcll}
\text{Imesatin} \;\;.\;.\;. & C_{16}H_6N_2O_2 & = & \overbrace{C_{16}H_5NO_4}^{\text{Isatin.}} & + \;\; H_3N - 2\,HO \\
\text{Imasatin} \;\;.\;.\;. & C_{32}H_{11}N_3O_6 & = & 2\,(C_{16}H_5NO_4) & + \;\; H_3N - 2\,HO \\
\text{Isamic acid} & HO, C_{32}H_{12}N_3O_7 & = & 2\,(C_{16}H_5NO_4) & + \;\; H_3N \\
\text{Amasatin or isamide} & C_{32}H_{14}N_4O_6 & = & 2\,(C_{16}H_5NO_4) & + \;\; 2\,H_3N - 2\,HO \\
\text{Isatimide} \;\;.\;.\;. & C_{48}H_{17}N_5O_8 & = & 3\,(C_{16}H_5NO_4) & + \;\; 2\,H_3N - 4\,HO.
\end{array}$$

Chlorisatin and dichlorisatin when heated with ammonia yield corresponding compounds.

(1291) *Isathyd* ($C_{16}H_6NO_4$).—This substance stands in the same relation to isatin that white indigo does to blue indigo; that is to say, it contains one equivalent more of hydrogen than isatin. In order to procure isathyd an alcoholic solution of isatin is mixed with one of hydrosulphate of ammonia, and set aside for a week in a closed bottle; crystals of sulphur are gradually deposited, mixed with prismatic needles of isathyd. The sulphur must be removed by digestion with bisulphide of carbon. A better method, however, consists in placing powdered isatin in a flask with a considerable quantity of water acidulated with sulphuric acid, then introducing a plate of pure zinc, and heating the whole to the boiling point. As the isatin becomes dissolved, it combines with the nascent hydrogen, and is converted into isathyd, which is deposited in the form of a crystalline powder. Isathyd is a greyish white, tasteless substance, which is insoluble in water, and but sparingly soluble in alcohol and in ether even at a boiling temperature: it is deposited from these solutions as they cool in minute oblique prisms. If heated, it softens and becomes decomposed, and acquires a violet brown tint. Boiling nitric acid colours it violet, and dissolves it. Isathyd yields various substitution products with chlorine and with bromine.

When a current of sulphuretted hydrogen is transmitted through a boiling concentrated alcoholic solution of isatin, the isatin is converted into isathyd, and this, at the moment of its formation, becomes decomposed, and ***bisulphisathyd***, a sulphuretted compound corresponding in composition to isathyd, is formed:—

$$\overbrace{C_{16}H_5NO_4}^{\text{Isatin.}} \quad + \quad HS \quad = \quad \overbrace{C_{16}H_6NO_4}^{\text{Isathyd.}} \quad + \quad S; \text{ and}$$

$$\overbrace{C_{16}H_6NO_4}^{\text{Isathyd.}} \quad + \quad 2\,HS \quad = \quad \overbrace{C_{16}H_6NO_2S_2}^{\text{Bisulphisathyd.}} \quad + \quad 2\,HO.$$

When the liquid has become clear by the deposition of the sulphur, the bisulphisathyd may be precipitated by the addition of water. It is a yellowish grey, tasteless powder, which softens at 212°; alcohol and ether dissolve it, but do not yield it in a crystalline form on evaporation.

Various other sulphuretted derivatives may be obtained from isatin (Laurent, *loc. cit.*)

(1292) *Indin* ($C_{32}H_{10}N_2O_4$).—This substance appears to be polymeric with indigo blue. It is of a beautiful rose-colour, is insoluble in water, and but sparingly soluble in alcohol and ether, even at a boiling temperature. In order to prepare indin, bisulphisathyd is triturated in a mortar for some minutes with a concentrated solution of potash, adding a few drops of the alkaline solution from time to time, until a rose-colour begins to show itself. Alcohol is then to be added in small quantities at a time, continuing to triturate the mass until the mixture has assumed a deep rose-colour. It is then to be diluted with alcohol, and the insoluble portion collected on a filter and washed first with alcohol, then with water. If this residue be dissolved in a concentrated solution of potash, black needles of *indinate of potash* ($C_{32}H_9KN_2O_4$) are deposited. They must be washed with absolute alcohol, and decomposed with a weak solution of hydrochloric acid. Pure pulverulent indin is left on washing the insoluble residue. *Nitrindin* $C_{32}H_8\,2\,(NO_4)N_2O_4$, *chlorindin* ($C_{32}H_8Cl_2N_2O_4$), and *bichlorindin* ($C_{32}H_6Cl_4N_2O_4$) are substitution compounds obtainable from indin.

Hydrindin ($C_{32}H_{11}N_2O_4$, Aq ?)—This substance appears to stand in a similar relation to indin that reduced indigo does to blue indigo. When the black solution of indinate of potash is heated with an excess of an alcoholic solution of the alkali, the colour gradually changes into a pale yellow, and on cooling deposits crystals of *hydrindinate of potash*. Water decomposes them, and leaves hydrindin in the form of a white powder, insoluble in water, and sparingly soluble in hot alcohol.

A number of other compounds have been obtained from indigo: they are described by Laurent, *loc. cit.*, and by Erdmann (*Journal für prakt. Chemie*, vols. xix., xxii., and xxiv).

(1293) 2. COLOURING MATTERS OF THE LICHENS.—Many of the lichens afford colouring matters which are of considerable importance. A yellow lichen common on old walls (*Parmelia parietina*) contains a colouring matter identical with that of the rhubarb root (1271), and the different varieties of *Usnea* and of *Evernia* furnish an analogous, straw yellow, crystalline substance, termed *usnic acid* ($HO,C_{38}H_{35}O_{13}$?) which is easily dissolved by ether; it yields red compounds with the alkalies. When boiled with an excess of alkali it furnishes a substance termed by Stenhouse *beta-orcin* ($C_{16}H_{10}O_4$?) The same compound is obtained by the distillation of usnic acid. These acids are unimportant as colouring matters and need not be further noticed here.

(1294) The red, violet, and blue colours, which are known in commerce under the names of *archil, cudbear,* and *litmus,* are supplied by different species of *Roccella, Variolaria,* and *Lecanora.* The *Roccella* tribe grow upon rocks on the sea-coast, in the Canary Islands, in Sardinia, and in Corsica, at the Cape of Good Hope, on the western coast of South America, and in various other parts of the world. The *Variolaria* abounds in certain parts of the Pyrenees, and of the Alps; and the *Lecanora tartarea* is abundant on the Swedish mountains.

None of these lichens furnishes the colouring matter ready formed; but they contain from seven to twelve per cent. of various colourless acids, such as the *erythric* ($C_{32}H_{16}O_{16}$?), *evernic* (HO, $C_{34}H_{15}O_{13}$?), and *lecanoric* acids (HO, $C_{32}H_{13}O_{13}$?); these bodies under the influence of alkalies are readily decomposed into new acids, which are characterized by the production of a violet colour with chloride of lime, and into a colourless neutral substance, termed *orcin* ($C_{14}H_8O_4$). Orcin is the true colour-producing body; under the influence of ammonia it absorbs oxygen, and is converted into *orcein* ($C_{14}H_7NO_6$), an azotized substance possessed of high tinctorial power.

In the preparation of *Archil* the lichens are first freed as far as may be from earthy impurities, and are made up into a paste with some ammoniacal liquid, such as urine to which a quantity of lime has been added, for the purpose of liberating its ammonia; the mixture is then exposed for some weeks to the air, moistening it from time to time with fresh quantities of the ammoniacal liquid. A paste is thus obtained of an offensive odour and of an intense violet-red colour; it constitutes the archil of commerce. *Cudbear* is obtained by a similar process from the *Lecanora tartarea;* the colouring-matter of these dye-stuffs consists chiefly of orcein. Cudbear is employed chiefly for woollen and silk goods, to which it imparts a brilliant but not very permanent dye, of various shades of violet, lilac, and purple.

(1295) *Litmus* is obtained principally from the *Roccella tinctoria:* it is prepared by a process similar to that used for archil, but is moistened with a mixture of carbonate of ammonia and carbonate of potash. During its preparation the mass at first assumes a red colour, but it ultimately becomes of an intense blue. It is made up with chalk or plaster of Paris into small cakes for the market. A small portion only of the colouring matter of litmus is soluble in water and in alcohol, but it is nearly all soluble in alkaline liquids. The chemical composition of litmus still demands further investigation. Kane (*Phil. Trans.*, 1840), states that litmus contains several principles; one is a red semi-solid substance, which he terms *erythrolein:* it is soluble in ammonia with a purple colour: another is *erythrolitmin,* which forms crystalline grains of a dark red colour, soluble in alcohol, but not in ether; it becomes blue by the action of potash: neither of these substances contains nitrogen. But the principal constituent of litmus consists of a third body termed *azolitmin,* in which nitrogen is present; it is insoluble in alcohol and in ether, and sparingly soluble in water; it is amorphous, and of a brown red colour. Ammonia dissolves it and forms a blue solution, which gives blue and violet lakes when mixed with the salts of several of the metals.

(1296) *Assay of Lichens for Colouring Matter.*—The different lichens contain variable amounts of colour-producing ingredients; consequently their commercial value is liable to great variation. Stenhouse estimates the comparative value of different samples by means of a standard solution of chloride of lime. A given weight of the lichens in powder is digested with slaked lime and water in order to extract the colorific acid, and on adding chloride of lime to this liquid a red colour is produced, which disappears in a few minutes, leaving a brownish yellow tint; fresh quantities of the chloride are added so long as this red coloration is produced by it. Another method also suggested by the same chemist consists in adding an acid to the solution of the lichen acids in lime water, and collecting and weighing the precipitate of the lichen acids. The colour-producing acids may be extracted by the following method (Stenhouse):—The pulverized lichens are mixed with water, and, after standing for an hour, a quantity of slaked lime is added, and the mixture is allowed to digest for some time; it is then placed in a linen filter supported in a tin vessel with a perforated bottom, and the liquid is gradually displaced by the cautious addition of water, the washing being continued so long as the filtrate yields the characteristic purple red colour with solution of chloride of lime. On the addition of hydrochloric acid to the filtered solution, the lichen acids are precipitated in the form of a white gelatinous deposit, from which the water may be removed by pressure. The acids may then be crystallized from warm alcohol, but they must not be boiled with alcohol, otherwise compound ethers would be formed, into the composition of which the acids enter. This remarkable power of etherifying alcohol is a striking chemical peculiarity of the lichen acids.

The formulæ which represent the composition of the numerous derivatives of the lichens are at present variously represented by different chemists. Those proposed by Gerhardt are founded chiefly upon the analyses of Schunck and of Stenhouse: they appear to explain in a simple manner most of the metamorphoses which the lichen acids undergo, and they agree with the actual results of analysis very nearly as well as the empirical formulæ adopted provisionally by Stenhouse and other chemists* who have specially examined these compounds:—

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* See Schunck (*Liebig's Annal.*, xli. 157; liv. 257; lxi. 64); Rochleder and Heldt (*Ib.* xlviii. 1); Stenhouse (*Phil. Trans.*, 1848, p. 63; 1849, p. 393).

	Gerhardt.		
Usnic acid	$C_{38}H_{16}O_{14}$	$C_{34}H_{17}O_{14}$	Stenhouse
Erythric acid . . .	$C_{32}H_{16}O_{16}$	$HO, C_{20}H_{10}O_{9}$	Do.
Picro-erythrin . . .	$C_{30}H_{20}O_{16}$	$C_{34}H_{24}O_{20}$	Schunck
Erythro-mannite . .	$C_{14}H_{16}O_{12}$, Aq	$C_{11}H_{14}O_{11}$	Stenhouse
Roccellinin	$C_{36}H_{16}O_{14}$	$C_{38}H_{17}O_{15}$	Do.
Evernic acid	$C_{34}H_{16}O_{14}$	$HO, C_{34}H_{15}O_{13}$	Do.
Evernesic do. . . .	$C_{18}H_{10}O_{8}$	$HO, C_{18}H_{9}O_{7}$	Do.
Lecanoric do. . . .	$C_{32}H_{14}O_{14}$	$HO, C_{18}H_{8}O_{8}$	Schunck
Alpha-orsellesic do. .	$C_{16}H_{8}O_{8}$	$HO, C_{16}H_{8}O_{7}$	Stenhouse
Orsellesic(lecanoric) ether	$C_{4}H_{5}O, C_{16}H_{7}O_{7}$	$C_{4}H_{5}O, C_{18}H_{8}O_{8}$	Schunck
Parellic acid	$C_{18}H_{6}O_{8}$	$HO, C_{21}H_{7}O_{9}$, Aq	Do.
Gyrophoric acid . .		$HO, C_{36}H_{17}O_{14}$	Stenhouse
Orcin	$C_{14}H_{8}O_{4}$, 2 Aq	$C_{16}H_{11}O_{7}$	Do.
Beta-orcin	$C_{16}H_{10}O_{4}$	$C_{38}H_{24}O_{10}$	Do.
Orcein	$C_{14}H_{7}NO_{6}$		

(1297) *Erythric Acid,* or *Erythrin* ($C_{32}H_{16}O_{16}$?).—This compound appears to be present in most of the lichens which yield archil. It is soluble in about 240 parts of boiling water, but is nearly insoluble in cold water; hot alcohol also dissolves it, and deposits the acid in stellate groups of needles. It is likewise soluble in ether. When heated in a tube it is decomposed, and orcin is sublimed. The alkalies dissolve it with facility. When boiled with baryta, a carbonate of this base is formed, and orcin is liberated:—

$$\overbrace{C_{32}H_{16}O_{16}}^{\text{Erythric Acid.}} = 4\,CO_2 + \overbrace{2\,(C_{14}H_8O_4)}^{\text{Orcin.}}.$$

By long boiling of the aqueous solutions of erythric acid, water is assimilated, and it is decomposed with evolution of carbonic acid into *picro-erythrin*:—

$$\overbrace{C_{32}H_{16}O_{16}}^{\text{Erythric Acid.}} + 4\,HO = 2\,CO_2 + \overbrace{C_{30}H_{20}O_{16}}^{\text{Picro-erythrin.}}.$$

Picro-erythrin ($C_{30}H_{20}O_{16}$?) is a colourless substance which is sparingly soluble in cold water, but very soluble in boiling water, from which, on evaporation, it may be obtained in confused crystals. It has a very bitter taste. Its solutions give a precipitate with subacetate of lead, but none with the neutral acetate: with perchloride of iron it produces a beautiful purple colour. If heated alone in a tube it yields a sublimate of orcin. Alkalies dissolve it readily without the aid of heat. Its ammoniacal solution quickly becomes red by exposure to the air. When boiled with milk of lime or with baryta water it is decomposed, carbonate of lime or of baryta is formed, and orcin and a new body termed *erythro-mannite* are produced:—

$$\overbrace{C_{30}H_{20}O_{16}}^{\text{Picro-erythrin.}} + 4\,HO = 2\,CO_2 + \overbrace{C_{14}H_8O_4}^{\text{Orcin.}} + \overbrace{C_{14}H_{16}O_{12}}^{\text{Erythro-mannite.}}.$$

Erythro-mannite, Pseudo-orcin, or *Erythro-glucin* ($C_{14}H_{16}O_{12}$ + Aq; Gerhardt), is probably homologous with mannite. It may be extracted from the solution of the *roccella* in lime water, by boiling it for some hours in an open capsule, and then removing the excess of lime by means of a current of carbonic acid. On evaporation a syrupy mass is obtained, consisting chiefly of orcin and erythro-mannite; the former may be extracted by means of ether or of alcohol. Erythro-mannite crystallizes from the residue in the course of a few days, and may be purified by washing it with cold alcohol and recrystallizing from boiling alcohol. Its aqueous solution deposits it in broad voluminous, brilliant crystals, belonging to the pyramidal system. Erythro-mannite is neutral to test papers; it is very soluble in water, and has a sweet taste, but it is not fermentable. When treated with fuming nitric acid kept cool, it yields an explosive compound, $C_{14}H_{10}(NO_4)_6O_{12}$, which corresponds to nitro-mannite (946): this body may be crystallized from its solution in boiling alcohol in brilliant laminæ, fusible at 142°.

(1298) *Evernic Acid* (HO, $C_{34}H_{15}O_{13}$?) occurs associated with usnic acid in the *Evernia prunastri*. It is scarcely soluble in water, even when at a temperature of 212°, but is readily soluble in alcohol and in ether; with potash and baryta it yields soluble crystallizable salts. When boiled with lime or baryta in excess orcin is formed, and a new acid termed *evernesic acid*:—

$$\overbrace{C_{34}H_{16}O_{14}}^{\text{Evernic Acid.}} + 2\,HO = 2\,CO_2 + \overbrace{C_{18}H_{10}O_8}^{\text{Evernesic Acid.}} + \overbrace{C_{14}H_8O_4}^{\text{Orcin.}}.$$

Evernesic acid does not yield orcin; ammonia does not produce any red colour with it; nor does chloride of lime yield with it a red or violet colour.

(1299) If the *Lecanora tartarea* and some other lichens be treated with ether, and the solution be evaporated, white crystals of *lecanoric acid** ($C_{32}H_{14}O_{14}$?) are deposited; this substance is nearly insoluble in cold water, but it is freely dissolved by hot alcohol and by ether; its solution reddens litmus. Perchloride of iron strikes a dull purple red with its spirituous solution. If boiled with alcohol it produces a true compound ether. The caustic alkalies dissolve lecanoric acid, and deprive it of carbonic acid, leaving *orcin* in solution. Orcin is also obtained by simply heating lecanoric acid and distilling. If lecanoric acid be treated with ammonia and exposed to the air, the acid combines with the elements of ammonia, and a purple compound is gradually formed, owing to the production of orcin.

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* Lecanoric acid, according to Gerhardt, is identical with the alpha and beta orsellic acids of Stenhouse.

Alpha-orsellesic Acid ($HO, C_{16}H_7O_7$) is one of the products of the decomposition of lecanoric acid when its solution is boiled for a short time with an excess of lime or of baryta; by prolonged boiling it becomes converted into orcin:—

$$\overbrace{C_{32}H_{14}O_{14}}^{\text{Lecanoric Acid.}} + 2\,HO = 2\,\overbrace{(C_{16}H_8O_8)}^{\alpha\text{ Orsellesic Acid.}};\ \text{and}$$

$$\overbrace{C_{16}H_8O_8}^{\alpha\text{ Orsellesic Acid.}} = 2\,CO_2 + \overbrace{C_{14}H_8O_4}^{\text{Orcin.}}.$$

When either lecanoric or erythric acid is boiled with alcohol for some hours orcin is separated, and a substance termed ***pseudo-erythrin*** or *lecanoric ether*, more properly *orsellesic ether* ($C_4H_5O, C_{16}H_7O_7$) is formed: it crystallizes in plates or needles, which may be purified by recrystallization from boiling water. It is scarcely dissolved by cold water, but is very soluble in alcohol and in ether, as well as in alkaline solutions, from which it is precipitated unaltered on the addition of an acid. Its ammoniacal solution, when exposed to the air, assumes a wine-red tint.

In certain cases Schunck found an acid which he terms *parellic acid* ($HO, C_{21}H_7O_9$, Aq ?), accompanying lecanoric acid; it is a fusible compound, which does not yield orcin when treated with alkalies. It crystallizes in brilliant, colourless, heavy needles, which are very sparingly soluble in cold water, but freely soluble in ether and in alcohol. The alcoholic solution has a very bitter taste; water precipitates the acid from it in a gelatinous form. It forms a white insoluble salt with baryta.

(1300) *Orcin* ($C_{14}H_8O_4$, 2 Aq; Gerhardt), *Sp. gr. of vapour* 5·7, corresponding to 3 volumes.—This substance appears to exist ready formed in several lichens, but it is generally procured by decomposing evernic, erythric, or lecanoric acid, by boiling it with an alkali. Stenhouse prepares orcin by boiling the solution obtained by treating one of the varieties of the *roccella* or *lecanora* with lime for some hours, and concentrating it by evaporation. The excess of lime must then be removed by means of a current of carbonic acid, and the filtered liquid evaporated to the consistence of a syrup; this residue must be treated with boiling alcohol, and allowed to crystallize; the red crystals thus obtained must be purified by recrystallization from their solution in ether. Orcin is a substance with a sweet but mawkish taste. It crystallizes with 2 Aq in colourless, quadrangular prisms, and is readily soluble in alcohol, ether, and water. When heated to 212° it melts and gives off its water of crystallization, and at 550° it may be sublimed unchanged. It is not susceptible of the vinous fermentation. In its anhydrous form it is metameric with saligenin. With persalts of iron it gives a dark red precipitate; it gives no precipitate with neutral acetate of lead, but with subacetate of lead a white precipitate is occasioned ($C_{14}H_6Pb_2O_4$, 2 PbO). With chloride of lime orcin gives a purple red colour, which quickly changes to a deep yellow. Nitric acid converts orcin into oxalic acid, and a resinous substance.

Orcein ($C_{14}H_7NO_6$).—If orcin be exposed in a shallow dish under a bell-glass with air to the vapour of ammonia, it yields a fine red colour; oxygen is absorbed, and a compound is obtained which has received the name of *orcein*:—

$$\overbrace{C_{14}H_8O_4}^{\text{Orcin.}} + H_3N + O_6 = \overbrace{C_{14}H_7NO_6}^{\text{Orcein.}} + 4\,HO.$$

The aqueous solution of the result of the foregoing reaction must be mixed with acetic acid, when orcein falls in red flocculi. Orcein is sparingly soluble in water, from which it is completely precipitated on the addition of a neutral salt. Alcohol dissolves it freely, forming a scarlet solution. It is sparingly soluble in ether. Potash and ammonia dissolve it readily, forming a splendid purple colour, which is the basis of the ordinary archil of commerce; the addition of common salt precipitates it from its solutions in the alkalies. With metallic salts its alkaline solutions yield beautiful purple lakes. The addition of acids restores its red tint, hence its value in the form of litmus as a test for free acids. If a solution of orcein be treated with hydrochloric acid and zinc in closed vessels it becomes colourless, but it resumes its red colour on exposure to the air.

Beta-Orcin ($C_{16}H_{10}O_4$?), the compound obtained by distillation of usnic acid (1293), is regarded by Gerhardt as a homologue of orcin: it is easily soluble in boiling water, alcohol, and ether; it has a slightly sweet taste. When mixed with ammonia it rapidly acquires a fine red tint. With caustic potash it yields a fine purple, and by chloride of lime its colour is instantly converted into a blood-red.

(1301) The vegetable colours are not the only ones which are used in dyeing; a beautiful blue is now prepared from ferrocyanide of potassium and the persalts of iron. A yellow is produced by chromate of lead, and an orange upon woollen and silk goods by means of concentrated nitric acid.

A variety of colours are used by the artist as pigments; most of these are obtained from the mineral kingdom: many of these mineral colours are wanting in transparency and brilliancy, but they are generally very durable. The pigments procured from the vegetable kingdom are more brilliant but less permanent, and in the small number of cases in which they are obtained from the animal creation they generally combine durability with brilliancy. Several of the pigments in common use, such as the preparations of lead, arsenic, and copper, are poisonous. Many of the metallic colours, particularly those which contain lead, are injured by exposure to sulphuretted hydrogen, and become black. Vegetable colours are especially prone to fade under the influence of atmospheric oxygen, aided by a strong light.

(1302) *Colouring Matter of Plants and of Flowers.*—*Chlorophyll,* as the green colouring matter so generally diffused through the vegetable kingdom is termed, appears to be of a resinous nature. It is soluble in alcohol and in ether, but insoluble in water. The alcoholic solution is of a beautiful green colour, and on evaporation leaves the chlorophyll in an amorphous state. If the leaves be treated with ether, the colouring matter is dissolved, but it is accompanied by a wax-like body, which is insoluble in cold alcohol. Chlorophyll is not known in a state of purity. When present in the leaf it undergoes various changes of colour, according to the plant in which it occurs. In autumn, before the leaves fall, it generally passes into yellow, as may be seen in the lime, the poplar, the horse chesnut, and the common laurel. In other cases the colour changes to red, of various shades, as in the Virginia creeper, the Spanish chesnut, and the sumach. The chemical changes which occur in these cases have not been satisfactorily explained.

Fremy and Cloez have examined the colouring matters of various flowers, and they consider that these tints may be referred to three distinct substances, one of which is of a blue or rose colour, while the other two are yellow. The blue or rose colour is produced by a compound which has been termed *cyanine,* the blue tint becoming red when exposed to the action of an acid. Red flowers have been observed to possess a juice the reaction of which is acid, whilst in blue flowers the juice is neutral. Cyanine may be obtained from the petals of the violet, or of the iris.

Xanthine is the name given to the yellow matter which is insoluble in water: the petals of the sunflower contain xanthine in abundance. The yellow substance which is soluble in water is termed *xantheine*: it becomes brown by the action of alkalies, and may be obtained from the yellow dahlia. None of these bodies, however, has been isolated in a pure condition, and there is considerable doubt whether the colours of the flowers of different plants be due uniformly to the same materials. The yellow colouring matters, however, are clearly of a nature different from that of the blues and reds. Many red flowers become blue and green as they wither, but they never become yellow. Blue flowers are also sometimes observed to fade into red before the colour disappears, but they never become yellow; and on the other hand, a yellow flower as it withers never becomes blue.

Dyeing and Calico Printing.

(1303) *Use of Mordants.*—Of the various colouring matters used in dyeing, some, like indigo and safflower, are capable of being permanently attached to the fabric, and of fully communicating their colour to it without the intervention of any other substance, and have hence been termed *substantive* colours; but the greater number of the colouring matters which are employed in the arts are removable by washing. Such is the case when calico, for example, is boiled in the madder vat, or when flannel is heated with infusion of cochineal. Hence it becomes necessary, in order to fix the colour upon the cloth, to employ various substances which possess a strong tendency to attach themselves to the fibres of the texture, and to combine chemically with the dye-stuff; they thus form the connecting link between the two. Bodies employed for this purpose are called *mordants*, and the colours which require such treatment are termed *adjective* colours. Various mordants are in use, some being better adapted to one dye, some to another. *Alumina*, in the shape of a mixture of alum and cream of tartar, is extensively employed for woollen goods and for silks; for calicoes acetate of alumina (1169), diluted till the solution has the sp. gr. 1·08, is much employed, especially for madder dyeing. It communicates to cloth impregnated with it a brown tint in the madder vat, if concentrated, and a red or pink if more dilute.

Peroxide of Iron is another mordant largely used; it is applied in the form of protacetate of iron, which is prepared by dissolving iron filings or nails to saturation in strong acetic acid, and the solution is then diluted till of the sp. gr. 1·05. When this mordant is used it is applied some time before the cloth is to be dyed; the cloth is then hung up for several days in rooms fitted up with open lath floors and lath supports provided with hooks, from which it is suspended in folds; the air thus has free access to it, and the protoxide of iron, by absorbing oxygen, is converted into peroxide, which is precipitated upon the cloth, in a form which is insoluble, owing to the want of acid to neutralize it. In this form, without any further addition it gives a buff colour. Oxide of iron is also largely used as a mordant, both for madder and logwood. *Peroxide of Tin* is another valuable mordant; it is generally mixed with the colour, both being put into the bath at once. Oxide of manganese, oxide of chrome, and some other metallic oxides, are also applied as mordants for particular purposes.

(1304) *Dyeing.*—The process of *dyeing* generally consists in the immersion of the mordanted goods in a solution of the colouring matter, the temperature of which is gradually raised to ebullition by the injection of steam, the cloth being *winced* through the mixture, by placing it upon a revolving spindle or windlass; each portion of the cloth is thus alternately raised out of and replunged into the bath, and a uniform application of the colour to every part is insured. In woollen goods the richest colours are obtained by dyeing the yarn previous to its being woven, since in this form it absorbs the colouring material much more readily than after it has been subjected to the mechanical operation of weaving and dressing; but this method of proceeding is more expensive than dyeing in the piece.

The following outline of the process adopted in dyeing Turkey red, abridged from the account given by Dr. Thomson, will afford some idea of the complicated, and apparently trivial circumstances requisite to produce a good dye:—

In order to remove the weaver's dressing, the cloth is first steeped for twenty-four hours at 120°, in a weak alkaline ley, containing 4lb. of potash to every 100lb. of cloth. It is then boiled with a solution of carbonate of soda, after which it is digested in an imperfect soap ley, composed of Gallipoli oil, sheep's dung, and a mixture of pearlash and carbonate of soda, in quantity much too small to saponify the whole of the oil. This oiling is repeated four or five times, allowing the cloth to become dry in the air between each immersion. The goods are next subjected to the action of a weak alkaline ley, in order to remove the excess of oil, and to prepare them for the operation of *galling*. Every 100lb. of cloth is then immersed in a bath containing twenty-five gallons of it through a warm solution of chloride of lime the chlorine will be disengaged upon the spots to which the acid was applied, and the colour will be removed at these parts of the cloth only. If the pattern discharged be required to be dyed again, the acid may be mixed with some suitable mordant—suppose it be acetate of lead; and after washing out the solution of the chloride of lime, the cloth may be passed through another liquid, such as bichromate of potash; in this case a yellow pattern, due to the formation of chromate of lead, would be produced. In some cases it is found to be more convenient to mordant the whole cloth in the first instance, and afterwards to discharge the mordant in patterns. Thus a piece of calico which has been mordanted by means of a mixture of alum and iron mordants may be discharged in patterns: by putting citric acid upon it, the mordant will be discharged upon those spots only; if it be then well washed and immersed in a logwood bath, it will come out dyed of a brown colour in every part except the places to which the citric acid was applied.

Occasionally with substantive colours, such as indigo, what are called *resist-pastes* are used: if, for instance, patterns be printed upon the cloth, with nitrate of copper properly thickened, and the goods thus prepared be passed through the indigo vat, the nitrate of copper will act by oxidizing the indigo in the parts to which the salt is applied, and the dye-stuff will not soak into the cloth in its reduced form at those points: hence, the colouring matter may be readily washed away from the spots to which the resist-paste was applied, whilst it remains fixed firmly everywhere else.

A peculiar modification of the mode of fixing the colours has received the name of *steam colour-printing*. For steam colours peroxide of tin is generally employed as the mordant. The perchloride of tin is decomposed by an excess of potash, which dissolves the precipitated oxide, and into this solution, when properly diluted, the cloth is dipped, and allowed to dry. After this it is immersed in very dilute sulphuric acid, to neutralize the potash, whilst the peroxide of tin remains attached to the fibre: the colours, properly thickened, are then printed on in patterns, and the whole exposed to the action of steam. At this temperature the colour combines completely with the mordant, producing a brilliant effect.

In preparing pyroligneous acid, wood which contains but little resin is used, and the condensation is more complete. The tar is of a different kind, and contains a variety of products, which have been already enumerated.

(1307) *Paraffin* (xCH), *Sp. gr.* 0·870.—Amongst the solid constituents of tar is a crystalline substance, which comes over during the last stages of the distillation. It fuses at 110°, and at a higher heat may be distilled unchanged. It is insoluble in water, but is taken up freely by ether, and less abundantly by alcohol. It burns with a bright flame; candles made of it burn like those made of the finest wax. The strongest acids and alkalies, and even chlorine, unless at a high temperature, are without effect upon it; hence it has received the name of *paraffin* (from *parum affinis*). The bodies termed *cerene* and *melene*, which Brodie obtained during the distillation of wax (1135), are very similar to this substance, and contain carbon and hydrogen in equal atomic proportions. It is probable that many substances termed paraffin consist of a mixture of several polymeric hydrocarbons, which form the higher terms of the series to which olefiant gas belongs. Paraffin is an abundant constituent of Rangoon petroleum, and is obtained in considerable quantity from the products of the distillation of peat.

Paraffin Oil.—Amongst the products of the distillation of the bituminiferous substance, known as *Boghead Cannel* (*note*, p. 98), is a large quantity of an oily matter, the proportion of which is greater, the lower the temperature at which the distillation is effected. This oil is almost entirely free from oxygen. When rectified, a volatile portion may be separated from it, which, according to G. Williams, contains several of the radicles of the alcohols, including tetryl and amyl. The compounds which come over at a higher temperature appear to belong to the hydrocarbons of the form of (C_nH_n). For practical purposes they may be separated into three portions, one of which remains liquid at very low temperatures. The second portion, which is distilled at a higher temperature, deposits crystals of a solid hydrocarbon (one of the forms of paraffin), when exposed to a great reduction of temperature, and the last portions of the distillate are semi-solid at ordinary temperatures. It is obvious, therefore, that the products of the distillation of this mineral contain a mixture of several substances, the less volatile of which are found by analysis to be polymeric varieties of hydrocarbons of the same class as paraffin. The less volatile liquid portion of the oil is extensively used under the name of *paraffin oil*, for the purpose of lubricating machinery, to which use it is admirably adapted, since it does not bec oxidized or thickened by exposure to the air, and it evapo but slowly.

(1308) *Pyrene and Chrysene.*—In the later stages of the tillation of fatty and of resinous bodies, and in that of coal t yellow powder is sublimed, which contains two substances, ter by Laurent pyrene and chrysene. *Pyrene* ($C_{30}H_{12}$) is solubl hot ether, and may be separated from chrysene by mean this solvent, which at a low temperature deposits it in mi scopic rhomboidal plates. It is insoluble in water, an destitute of odour; it fuses at about 350°, and may be dist unaltered. *Chrysene* $(C_{12}H_4)_2$? is a crystalline substance beautiful yellow colour. It is inodorous, insoluble in water alcohol, and only slightly soluble in ether: boiling oil of tur tine dissolves it more readily than ether. It fuses at about and is partially decomposed when distilled.

(1309) *Pyroxanthin* ($C_{21}H_9O_4$? Gregory).—This substanc discovered by Scanlan amongst the products of the actio potash upon crude wood-spirit. When crude wood-spirit is fied with lime a dark brown residue remains in the retort, w when treated with hydrochloric acid leaves a brown inso matter, consisting of pyroxanthin and a resinous substance. this residue be boiled in alcohol it is in great measure disso and crystals of pyroxanthin are deposited as the liquid cools. crystallizes in long yellow needles, which are insoluble in w and in alkaline solutions, but soluble in hot alcohol, ether, acetic acid. It fuses at 291°, and may be sublimed in a cur of air at 273°. If it be sublimed in a closed tube it under partial decomposition. It is soluble in sulphuric acid with a bluish red colour, and in hydrochloric acid with a fine pu which soon passes into dark brown. Pyroxanthin appears to the result of the action of potash upon one of the tar oils, w Voelckel has hence termed *pyroxanthogen*.

(1310) *Eupion.*—When the tar of hard woods is submi to distillation, an acid liquid comes over, upon the surface which a light yellowish oil floats; and on continuing the disti tion a volatile oil, which is heavier than water, passes over. most volatile portion of the lighter oil consists principally hydrocarbon, to which Reichenbach gave the name of *eu* (C_5H_6), *sp. gr.* 0·655. It boils at 116°. Frankland consi eupion to consist principally of hydride of amyl.

The less volatile portions of the lighter oil contain wood spi acetone, and the hydrocarbons benzole, toluole, and xylole; these hydrocarbons may be removed by agitation with sulphuric acid, with which they form colligated acids. The heavier oil, which is of a yellow colour, also contains small quantities of the foregoing compounds: it is partially soluble in potash, and amongst the constituents of the portion which thus combines with the alkali, are *kreasote* and *kapnomor*.

(1311) *Kreasote* ($C_{24}H_{16}O_4$? Gorup Besanez; or $C_{16}H_{10}O_2 = HO, C_{16}H_9O$?) *Sp. gr.* 1·057 (from κρέας flesh, σώζω to preserve).—Considerable doubt exists as to the exact composition of this interesting substance. Much of the kreasote of commerce is simply carbolic (phenic) acid; but the true kreasote of Reichenbach is quite a distinct body. It is to this latter substance that wood-smoke owes its characteristic odour and antiseptic qualities.

Preparation.—The process of purifying kreasote is tedious and troublesome. The heavier portions of the oil obtained from wood tar, after being washed with a solution of carbonate of soda, are submitted to distillation, by which they are further separated into a portion lighter than water, and into another which sinks in this liquid. This heavier oil is then treated with a solution of potash of sp. gr. 1·12. By this means the kreasote is dissolved, and the greater part of the hydrocarbons which accompanied it are separated. The alkaline solution, after being decanted from the hydrocarbons, is boiled gently in an open basin, with a view to oxidize a portion of the impurities. When cold, dilute sulphuric acid in slight excess is added to the liquid, by which means the kreasote is set at liberty. It is, however, far from being pure, and must be redistilled with water, again treated with concentrated solution of potash, then with dilute sulphuric acid, and then redistilled with water. This series of operations is to be repeated so long as any separation of hydrocarbons is effected Lastly, the kreasote must be digested upon chloride of calcium, and distilled by itself. It may be regarded as pure if its boiling point be constant at 398°, and if it does not become brown when kept.*

Properties.—Kreasote, when pure, is a colourless oily liquid of high refractive power; it boils at 398° (Reichenbach). It is not easily inflamed, but when kindled it burns with a smoky flame.

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* By long boiling with potash the kreasote appears to undergo oxidation, a portion of its hydrogen being removed, whilst the quantity of oxygen is increased (Gorup Besanez).

Its taste is burning, and its odour extremely pungent and peculiar; if swallowed in doses of more than a few drops it acts as a poison. Kreasote is sparingly soluble in water, to which it communicates its peculiar odour and pungent taste. It is soluble freely in acetic acid, alcohol, and ether, as well as in benzole and bisulphide of carbon. It combines with potash, and forms a crystalline compound with it; solution of ammonia also dissolves it. Kreasote produces the immediate coagulation of albumen. It is the most powerful antiseptic known. Meat that has been plunged into a solution containing 1 per cent. of kreasote gradually becomes dry and hard on exposure to the air, and acquires the flavour of smoked meat, but does not become putrid. A considerable portion of kreasote is held in solution in the crude pyroligneous acid obtained during the destructive distillation of wood; and on saturating this acid at 167° with sulphate of soda, an oily matter which contains a large proportion of kreasote, is separated. Crude pyroligneous acid, on account of the kreasote which it contains, is frequently employed for preserving hams and salted provisions, to which it communicates the same flavour as if they had been exposed to wood smoke.

Kreasote when largely diluted is sometimes given internally in order to check obstinate vomiting. If applied in a concentrated form to the exposed pulp of a carious tooth, it frequently affords instant relief in cases of acute toothache. It is also a valuable application, in a very diluted form, in some cases of fœtid ulcers, and in many cutaneous affections. If applied to the skin in a concentrated state it produces a white spot, the skin becomes disorganized, and peels off without any attendant inflammation. Kreasote dissolves many organic bodies, such as camphor, the fatty and volatile oils, and many of the resins.

It is not improbable that kreasote may be a homologue of phenic acid, and that its true formula may be $C_{16}H_{10}O_2$. Phenic acid, when decomposed by a mixture of chlorate of potash and hydrochloric acid, yields perchlorokinone or chloranile (1127). Kreasote, when treated in a similar manner, furnishes a resinous mass, which after digestion with cold alcohol, leaves a compound resembling chloranile in appearance and properties ($C_{26}H_6Cl_6O_6$? Gorup Besanez). This new body crystallizes in brilliant, golden yellow plates; it is insoluble in water, sparingly soluble in cold alcohol, and freely soluble in ether: it may be sublimed at about 360°. Gerhardt has shown that the more probable formula $C_{16}H_4Cl_4O_4$ corresponds equally well with the results of its analysis, and in that case the compound would be homologous with chloranile, and would contain 2 (C_2H_2) more than the latter body.

(1312) *Kapnomor* ($C_{20}H_{11}O_2$? Voelckel; from καπνὸς smoke and μοῖρα a part); *Sp. gr.* 0·995.—This is a colourless oil of peculiar odour, which boils at about 360°. It is insoluble in water and in a solution of potash, but it is partially soluble in an alkaline solution of kreasote. It is soluble in sulphuric acid with a purplish red colour, and forms with it a colligated acid. Nitric acid converts it into oxalic and carbazotic acids, and another crystallized body which has not been examined. Kapnomor is obtained by distilling the crude solution of kreasote in potash with water: it passes over with the vapour of water.

Reichenbach has described various other compounds from tar, under the names of *pittacal*, a solid compound of a deep blue colour; of *picamar*, an oily body of sp. gr. 1·10, which has a very bitter taste, and forms a crystalline compound with potash; and of *cedriret*, which crystallizes in orange-red needles from a solution of persulphate of iron, and is dissolved with a blue colour in oil of vitriol; the properties of all these bodies have, however, been but incompletely examined.

(*b*) *Products of the Distillation of Pit-coal.*

(1313) The products of the distillation of pit-coal are still more numerous than those of wood; and they are invested with a special interest, owing to their intimate connexion with the manufacture of coal gas.

When a bituminous coal is burned in the open air, the principal products of the combustion are carbonic acid and water, with small quantities of ammonia and sulphurous acid, derived from the azotised constituents, and the pyrites contained in the coal; a certain portion of carbon in a finely-divided form escapes combustion, and constitutes the soot or visible smoke of a coal fire. When the decomposition of the coal is effected in vessels from which air is excluded, the products are much more numerous and complicated. A large amount of volatile matter is expelled, partly in the form of uncondensable gases, and partly in the form of vapours, which, when reduced to the ordinary temperature of the air, constitute liquids or solids, whilst a large proportion of the combustible material remains behind in the retort, and forms a light porous variety of coke, known as *gas coke.*

Amongst the gaseous products the most important are marsh gas, olefiant gas, hydrogen, carbonic oxide, carbonic acid, sulphuretted hydrogen, and ammonia. The liquid portions contain water, and various forms of hydrocarbon, such as benzole, toluole, and cumole, which constitute the chief ingredients of the liquid termed *coal naphtha;* besides which there is a large quantity of a dark viscous matter, known as *coal tar,* the nature of which will be more particularly considered hereafter (1315).

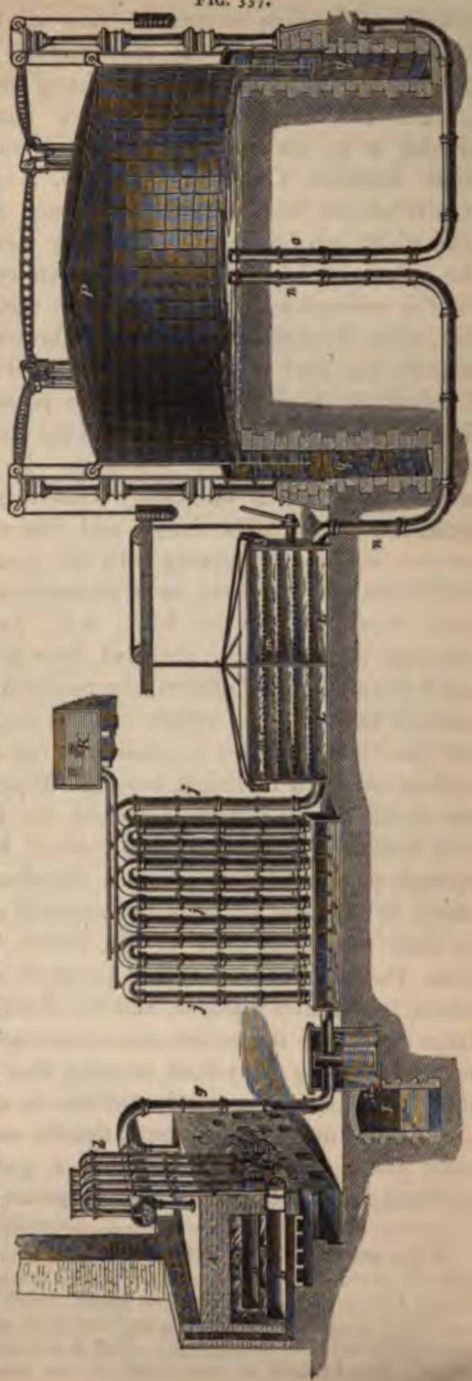
When coal gas is to be employed for the purpose of illuminating the interior of a dwelling-house, it is not sufficient to condense the tar, the water and other liquid products, but it becomes necessary to remove a number of gaseous compounds before it can be burned with comfort, or even with safety to the health of the inmates. The impurities of which it is of most importance to deprive it are sulphuretted hydrogen and ammonia; in addition to which carbonic acid and a small quantity of cyanogen are always removed during the purification. This purification is effected by submitting the gas to the action of certain chemical agents, such as lime, hydrated oxide of iron, and dilute sulphuric acid.

The illuminating power of coal gas is due chiefly to light carburetted hydrogen, olefiant gas, and to a small quantity of the vapour of naphtha and other volatile liquefiable compounds of carbon and hydrogen. The hydrogen and carbonic oxide are not only destitute themselves of any illuminating power, but they reduce the light of the gas with which they are mixed: there is however no means of getting rid of these useless gases; care should therefore be taken to produce as small an amount of them as possible during the process of carbonization.

(1314) *Manufacture and Purification of Coal Gas.*—The earliest attempts at illumination by means of coal gas were made by Mr. Murdoch, during his residence in Cornwall, about the year 1792, and he subsequently further carried out his plan, so as to illuminate a large portion of the manufactory of Boulton and Watt at Soho, at the celebration of the peace of Amiens in 1802. Ten years afterwards the Chartered Gas Company, which made the first great experiment of lighting the streets by gas, was incorporated; and from that day to the present the employment of gas as a convenient and economical means of illumination has been steadily increasing. At the present time every large manufacturing town, and many of the smaller towns, in Great Britain are lighted by gas, and the use of gas is general in the principal cities of the Continent.

The proportion in which the different products of the distillation of coal are obtained, varies greatly according to the kind

FIG. 337.



of coal employed, and the temperature at which the distillation is conducted. The coal best suited to the manufacture of gas for illuminating purposes is of the variety known as bituminous (951). Anthracite is unfit for this use. The kind of coal employed in London for gas making is principally that of the Durham coal field, or *Newcastle* coal. A ton of good coal of this description yields on an average in London about 9250 cubic feet of gas of sp. gr. of 0·410, and furnishes nearly a chaldron of coke weighing about 13 cwt. In coking, from 20 to 35 per cent. of fuel in proportion to the coal used (according to the judgment used in constructing the furnace) is employed. The Scotch coals furnish a gas of much higher illuminating power than that of the Newcastle coal, and of greater specific gravity, owing to the presence of a larger proportion of the vapours of the volatile hydrocarbons, though the quantity is a little smaller, and the coke produced is of an inferior quality.

Fig. 337 gives a general view of the arrangement of the apparatus required in the manufacture and purification of coal gas, and the following is an outline of the process adopted:—

Pit coal is heated in hollow flattened cylinders of iron or clay B B, set in stacks of three or five, arranged in long brick furnaces, A A. The mouths, *c c*, of these cylinders or retorts project from the brickwork, and are fitted with moveable lids, which can be closed air-tight by means of clay luting. From the upper side of the projecting extremity of each retort, a tube, *d*, for the conveyance of the gas, passes vertically upwards for a few feet, then forming an arch, dips downwards, terminating at *e*, beneath the level of the liquid contained in a long and wide pipe, *f*, called the *hydraulic main*, which passes horizontally along the front of the range of furnaces. This pipe is kept constantly half full of tar and condensed moisture. By this means the opening into each retort is effectually closed by a water valve, which permits a charge to be drawn and renewed in any one or more retorts, without interfering with the operation of those which are still in action. The tar, as it accumulates in the hydraulic main, flows over into the *tar wells*, H, I. In about four hours after charging the retort, the coal will have given off nearly all its gas, and a fresh charge of coal will be required; but it is not an unusual practice to charge the retorts only at intervals of six hours, since the gas, though poorer in quality, is increased in quantity, and the coke is improved by longer heating. When a charge is to be drawn, the mouth of the retort is opened, and the coke raked into large iron boxes, in which it is extinguished by pouring water over it. A fresh supply of coal is then introduced by means of a long scoop, so that the whole of the required quantity of coal is placed at once upon the floor of the retort, which is at a bright red heat. The door, which has been prepared with fresh luting upon its edges, is instantly replaced, and the distillation proceeded with. In large gas works the retorts are so arranged that a fresh set shall require charging every hour, in order that the gas which is produced shall at all times be nearly uniform in quality.*

Having deposited in the hydraulic main most of the tar and some water, containing in solution a good deal of ammonia and hydrosulphate of ammonia, the gas passes next through the pipe, *g*, to the *refrigerators* or *condensers*, *j j*, a series of serpentine or contorted tubes, which are kept cool by the extent of surface which they expose to the air, and the temperature of which, when necessary, may be reduced still further, by allowing cold water from the cistern, K, to flow over their exterior: here most of the remaining tar and aqueous vapour become separated. From the condenser the gas passes to the lime *purifiers*, L L′, which consist of cast-iron vessels containing a number of horizontal perforated shelves, *m m*, arranged one above another; upon these shelves dry slaked lime is placed, to the depth of about five inches. The gas enters at the bottom of the purifiers, and rises on one side through each layer of lime in succession,* descending on the other side of the purifier till it makes its exit at *n*. In these purifiers the gas loses carbonic acid, sulphuretted hydrogen, sulpho-cyanogen, cyanogen, and traces of naphthalin which are still suspended in it; finally it is caused to pass in bubbles through dilute sulphuric acid, with the view of removing the last portions of ammonia; but this part of the apparatus is not represented in the figure.

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* The gas first given off is the best, and also the largest in quantity, the coal not having had time to rise to the full temperature of the retort. If the charge be exposed to heat for five hours, much of the gas in the last hour and a half consists of hydrogen and carbonic oxide, the coal having become thoroughly red hot throughout. The following details will illustrate these points. Two bushels of cannel coal, or the usual charge of a moderately-

In many works the process of washing with acid is superseded by the use of an apparatus termed a *scrubber*, consisting of a tower, the interior of which is filled with small coke resting upon perforated shelves; through this mass of porous material a constant supply of fresh water is maintained, and by this arrangement the gas, which enters at the bottom of the tower, is exposed to a large absorbent surface, and the ammonia is effectually removed. This washing, however, somewhat diminishes the illuminating power of the gas, by removing a portion of the vapour of some of the more condensable hydrocarbons which are held in suspension.

A mixture of hydrated oxide of iron and moistened saw-dust is now extensively substituted for slaked lime in the purifier (636);

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sized retort, were carbonized at a full cherry-red heat, and the quantity of gas produced was as follows:—

	Cubic Feet.	Sp. Gr.
In the first hour	345	0·677
2nd	203	0·419
3rd	118	0·400
4th	54	0·322
5th	20	

The gas amounted in all to 740 cubic feet; but it will be observed that the quantity of gas per hour, as well as the specific gravity, continued to diminish as the experiment proceeded. This was due to the diminution in quantity of the vapour of the heavy hydrocarbons, and the increase in the amount of free hydrogen.

* Sometimes the lime is made into a thin cream by admixture with water, and the gas is caused to stream in bubbles through the mixture, but generally the lime is employed in the form of a slightly damp powder.

various other substances are also occasionally employed with a view of effectually arresting the sulphuretted and ammoniacal impurities. The gas, after it has been thus purified, is stored up for use in immense reservoirs or gasometers of metal, P, each consisting of a large bell of sheet iron, inverted in a brickwork tank, *q*, filled with water, in which the bell rises and falls. The bell is nearly counterpoised by weights attached to chains, which pass over pulleys suitably supported. The pressure, which is not usually allowed to exceed that of a column of water two or three inches in height, drives the gas along the pipes or *main, o o*, by which it is distributed to the various consumers.

In the foregoing process one of the points of greatest importance is the due regulation of the temperature during the distillation. The retorts should be heated to a bright cherry-red. If they be insufficiently heated, the products contain a large quantity of the vapours of condensable hydrocarbons, which collect in the gasometers and the distributing pipes, and occasion much loss and inconvenience: whilst if the temperature be too high, or if the gas after its production be allowed to remain long in contact with the highly heated surface of the retort, it undergoes partial decomposition; a portion of its carbon is deposited and forms a dense layer upon the interior of the retort, which it gradually chokes up, and at the same time the illuminating power of the gas is proportionately diminished by the loss of this carbon.

In addition to this inconvenience, bisulphide of carbon is apt to be formed in small quantity if the distillation be conducted at too high a temperature, and no means are as yet known by which this body can be removed. When gas which contains this impurity is burned, it gives rise to the production of a minute quantity of sulphuric acid, which gradually accumulates on the furniture of the building, on the bindings of books, &c., and slowly corrodes and otherwise injures them.

(1315) *Compounds of Coal-tar.*—Coal-tar varies in density from 1·120 to 1·150; the lightest tar containing the largest proportion of liquid oils. Of the substances contained in coal-tar some are basic, and some acid, but the principal portion consists of neutral or indifferent bodies.

The bases include ammonia, aniline, picoline, quinoline, and pyridine. (1064 *et seq.*) Among the acids, the acetic is present in small amount, but the most important is phenic acid, the carbolic acid of Runge. This chemist also mentions two other acids, termed *rosolic* and *brunolic* acids, which [illegible] been minutely examined.

The neutral substances contain several hydrocarbons, including benzole, toluole, cumole, and cymole, which are among the liquid constituents; whilst naphthalin, paranaphthalin, chrysene, and pyrene are among those which are solid at ordinary temperatures.

The distillation of coal-tar is conducted on an extensive scale, as a separate branch of trade. The operation is performed in large iron retorts upon quantities of several hundred gallons at a time. The first portions that are volatilized consist chiefly of ammonia accompanied by some permanent gases which have been dissolved by the liquid hydrocarbons. As the temperature rises, water charged with various ammoniacal salts comes over, and a fœtid brown oil gradually collects upon the surface of the water in the receiver. As the distillation proceeds, water ceases to come over, and the quantity of this oil increases, its density continuing to augment until its specific gravity exceeds that of water. The light oil amounts generally to from 5 to 10 per cent. of the tar. This lighter oil when rectified constitutes *coal naphtha*. By continuing the distillation a yellow heavy fœtid oil, technically known as *dead oil*, is obtained, the amount of which seldom exceeds 30 per cent. of the quantity of tar employed. In the latter stages of the operation, naphthalin is abundant in the distillate, and the oil becomes semi-solid as it cools. The black residue in the retort solidifies on cooling, and forms *pitch*, which is employed in the preparation of asphalt, and as a colouring ingredient in the production of a coarse black varnish, used for protecting iron-work from rust. If it be desired to carry the distillation further, a much higher temperature is required, when the pitch in its turn undergoes decomposition, and yields a product which, when cool, has the consistence of butter; it consists chiefly of paranaphthalin. At a still more advanced stage of the process, the distillate acquires a yellow colour, and assumes the appearance of a resin, and as the temperature of the retort approaches a red heat the vapours produced become condensed in the form of a bright orange-coloured powder which is free from odour, and when pressed, agglutinates into a viscous mass. This substance consists chiefly of the chrysene and pyrene of Laurent. The residue in the retort after it has ceased to give off volatile matters, forms a hard porous coke which is difficult of combustion.

The heavy coal oil is seldom submitted to further purification. It contains phenic (carbolic) acid, aniline, quinoline, and a variety of other bodies, consisting chiefly of hydrocarbons, which boil cumole, was found by Cahours among the products of the distillation of wood.

It would be easy, in connexion with these hydrocarbons, to form a table, of which the following is a fragment, constructed on the same principle as that given at pp. 32 and 33. The compounds of the various series of which it consists, with the exception of the derivatives of benzole, have been, however, only incompletely examined :—

Homologous Derivatives of Coal-tar Hydrocarbons.

Hydride. $C_nH_{n-7}, H.$	Chloride. C_nH_{n-7}, Cl	Nitro-compound C_nH_{n-7}, NO_4	Dinitro-comp'd. $C_nH_{n-6}\,2(NO_4)$	Amide-base. $C_nH_{n-7}, H_2N.$	Acid. HO, C_nH_{n-7}, O
Benzole. $\overbrace{C_{12}H_5, H}$	Chlorobenzole $\overbrace{C_{12}H_5Cl}$	Nitro-benzole. $\overbrace{C_{12}H_5, NO_4}$	Dinitrobenzole. $\overbrace{C_{12}H_4(NO_4)_2}$	Aniline. $\overbrace{C_{12}H_5, H_2N}$	Phenic Acid. $\overbrace{HO, C_{12}H_5, O}$
Toluole. $\overbrace{C_{14}H_7, H}$	Chlorotoluole $\overbrace{C_{14}H_7, Cl}$	Nitro-toluole. $\overbrace{C_{14}H_7, NO_4}$	Dinitrotoluole. $\overbrace{C_{14}H_6(NO_4)_2}$	Toluidine. $\overbrace{C_{14}H_7, H_2N}$	Kresylic Acid. $\overbrace{HO, C_{14}H_7, O}$
Xylole. $\overbrace{C_{16}H_9, H}$		Nitro-xylole. $\overbrace{C_{16}H_9, NO_4}$		Xylidine. $\overbrace{C_{16}H_9, H_2N}$	Kreasote (?) $\overbrace{HO, C_{16}H_9, O}$
Cumole. $\overbrace{C_{18}H_{11}, H}$		Nitro-cumole. $\overbrace{C_{18}H_{11}, NO_4}$	Dinitrocumole. $\overbrace{C_{18}H_{10}(NO_4)_2}$	Cumidine. $\overbrace{C_{18}H_{11}, H_2N}$	
Cymole. $\overbrace{C_{20}H_{13}, H}$		Nitro-cymole. $\overbrace{C_{20}H_{13}, NO_4}$		Cymidine. $\overbrace{C_{20}H_{13}, H_2N}$	

The hydrocarbons enumerated in the first column of the foregoing table, are supposed to be hydrides of particular radicles. These supposed radicles, viz., *phenyl* $(C_{12}H_5)_2$, *toluyl* $(C_{14}H_7)_2$, *xylyl* $(C_{16}H_9)_2$, *cuminyl* $(C_{18}H_{11})_2$, and *cyminyl* $(C_{20}H_{13})_2$, have not hitherto been isolated. Their oxides, which would correspond to the ordinary ethers, are also unknown; compounds, however, have been formed, which appear to contain oxide of phenyl in combination with acids; such, for example, as the following :—

Benzoate of phenyl . .	$C_{12}H_5O, C_{14}H_5O_3$	Laurent and Gerhardt.
Acetate of phenyl . . .	$C_{12}H_5O, C_4\,H_3\,O_3$?	Williamson and Scrugham.
Phosphate of phenyl . .	?	
Cuminate of phenyl . .	$C_{12}H_5O, C_{20}H_{11}O_3$	

Benzole is a compound of considerable interest and importance.

It belongs to a group known as the *phenic* series. We shal therefore, describe its properties, and that of some of its derivatives, including carbolic acid, and shall afterwards proceed t notice briefly some of the other hydrocarbons, among whic naphthalin is the most remarkable.

1. *Benzole.—Phenic Series.*

(2317) Benzole; *Benzine* or *Phene* ($C_{12}H_6$); *Sp. gr. of liqui* 0·85 at 60°; *of vapour* 2·77.—This is a very limpid, colourle liquid, of a peculiar and rather agreeable odour. If exposed to a cold of 32°, it solidifies in transparent crystals, grouped like fe leaves, or into masses resembling camphor, which melt at 40°. It boils at 177°, and emits a highly inflammable vapour, whic burns with a white smoky flame, depositing large quantities o carbon. If its vapour be transmitted through red-hot tubes it i decomposed, and a large quantity of carbon is deposited. It is n soluble in water, but is freely soluble in alcohol, ether, oil of turpentine, wood spirit, and acetone. When hot it dissolves sulphur, phosphorus, and iodine, and deposits the greater portion on cooling It is also an excellent solvent for caoutchouc and gutta perch and on evaporation it leaves them with their peculiar physical characters unaltered. Benzole also dissolves wax, camphor, and fatty bodies with facility. Its solvent power for fats and oils enables it to be used with advantage for removing grease stains from articl of silk or woollen. Benzole does not dissolve copal or resins wit facility, but if these bodies be exposed to its vapour at a high temperature they are gradually dissolved by it.

Benzole was originally obtained by Faraday from the liquid produced by the compression of oil gas, and was termed *bicarburet of hydrogen*. Subsequently the liquid procured by Mitscherlich from the distillation of benzoic acid with an excess of lime, by him termed *benzine*, was found to yield the same body, $HO, C_{14}H_5O_3 + 2\,CaO = 2\,(CaO, CO_2) + C_{12}H_6$; and recently, Mansfield has obtained it in large quantity from the more volatile portions of coal naphtha. It may also be obtained, mixed with other products, by several other processes, such as the distillation of phthalic acid with lime, and the dry distillation of kinic acid. Benzole may easily be procured in small quantities by exposing a mixture of one part of benzoic acid with three parts of quicklime, to a moderate heat gradually applied; the distillate should be agitated with a weak solution of potash, and the benzole which rises to the surface be dried by digestion upon chloride of calcium;

after which it may be obtained pure by redistillation. Benzoic acid yields about a third of its weight of benzole.* When benzole is required in considerable quantity, its cheapest source is coal naphtha, although on a small scale its purification is tedious. Mansfield, after purifying it by repeated rectifications, takes advantage of its power of solidifying at 32°, in order to free it from the hydrocarbons which accompany it, and which remain liquid at that temperature. By operating in this way upon two gallons of naphtha, a pint of pure benzole was procured.

(1318) *Hydrocarbons homologous with Benzole.—Toluole,* or *benzoene,* is one of the products of the distillation of balsam of tolu, and it appears to be identical with the *retinaphtha* obtained by Pelletier and Walter, from the distillation of rosin (1253). *Xylole* was found by Cahours, mixed with toluole, cumole, and cymole, among the oils which are separated from crude wood spirit by the addition of water. *Cumole* may also be obtained by the distillation of cuminic acid with an excess of quicklime: it appears to be identical with the *retinyl* of Pelletier and Walter. *Cymole* is present in essence of cummin, and it may also be obtained by distilling camphor with anhydrous phosphoric acid, or with chloride of zinc. These hydrocarbons are not, however, of sufficient importance to require any lengthened description in this work. In the following table their boiling points and densities are compared with those of benzole:—

Hydrocarbon.	Formula.	Boiling point, °F.	Specific Gravity.	
			Liquid.	Vapour.
Benzole . .	$C_{12}H_6$	177°	0·85	2·77
Toluole . .	$C_{14}H_8$	230°	0·87	3·26
Xylole . .	$C_{16}H_{10}$	263°		
Cumole . .	$C_{18}H_{12}$	299°		3·96
Cymole . .	$C_{20}H_{14}$	341°	0·861	4·59

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* If benzoate of lime be distilled with one-tenth of its weight of quicklime, it yields a red liquid which, when submitted to redistillation, first yields benzole; and when the temperature rises to 599° a compound termed *benzo-phenone* ($C_{12}H_5 . C_{14}H_5O_2$) passes over; this substance on cooling solidifies into a mass of straw yellow crystals, which may be purified by recrystallization from ether. When pure it forms beautiful colourless crystals, belonging to the oblique system. It melts at 115°, and boils at 599°; it has an agreeable ethereal odour. Benzophenone may be regarded as benzole, in which the place of an equivalent of hydrogen has been supplied by that of an equivalent of benzoyl, or as a combination of benzoyl with phenyl. When heated with a mixture of hydrate of potash and lime, it is decomposed into benzole and benzoate of potash:—

$$C_{12}H_5 . C_{14}H_5O_2 + KO,HO = C_{12}H_5 , H + KO, C_{14}H_5O_3.$$

(1319) *Other Compounds of Benzole.*—Benzole yields direct compounds with chlorine and bromine, $C_{12}H_6Cl_6$ and $C_{12}H_6Br_6$ when exposed to the sun's light in contact with these halogens. These substances present a certain analogy with Dutch liquid, and when decomposed by an alcoholic solution of potash, yield compounds which contain $C_{12}H_3Cl_3$ and $C_{12}H_3Br_3$.

Sulphuric acid forms a compound acid with benzole, termed *hyposulphobenzidic* or *sulphobenzolic acid* ($HO, C_{12}H_5, S_2O_5$): it furnishes readily crystallizable salts. If benzole be treated with anhydrous sulphuric acid a viscid mass is produced, which may be dissolved in a small quantity of water, but on the addition of a considerable amount of water, sulphobenzolic acid remains in the liquid, and a sparingly soluble crystalline body is separated. This crystalline body is termed *sulphobenzide* ($C_{12}H_5SO_2$); it may be purified by crystallization from ether: it is fusible at 212°, and may be distilled unaltered at a much higher temperature. Hofmann and Buckton have lately obtained a sulpho-acid with a larger proportion of sulphuric acid, termed *disulphobenzolic acid* ($2\ HO, C_{12}H_4S_4O_{10}$; page 305), by heating benzonitrile with fuming sulphuric acid.

(1320) *Nitrobenzole* or *nitrobenzide* ($C_{12}H_5NO_4$), *Sp. gr. of liquid* 1·209; *of vapour* 4·4.—Benzole is remarkable for the facility with which it yields substitution compounds with peroxide of nitrogen. If benzole be added, in small portions at a time, to warm fuming nitric acid, it is dissolved, and on cooling, or on being diluted, is separated in the form of a yellow oil, which may be purified by washing, first with water, and then with a weak solution of carbonate of soda.

Nitrobenzole is a yellowish oil, which becomes solidified in needles when exposed to a temperature of 37°. It boils at 415°, and may be distilled unaltered; it has a very sweet taste, and an odour resembling that of bitter almonds. It is used in perfumery under the name of *Essence of Mirbane*. Nitrobenzole is soluble in alcohol and in ether, in all proportions. If its alcoholic solution be saturated with ammonia, and then with sulphuretted hydrogen, sulphur is deposited, and aniline is formed; aniline is also obtained from it still more readily by adding nitrobenzole to a mixture of equal parts of alcohol and hydrochloric acid, and introducing fragments of zinc, or by the process of Béchamp, with protacetate of iron (page 254). The successive formation of nitrobenzole and of aniline may be employed as a test for the presence of benzole in oils:—a few drops of the suspected liquid are to be heated gently with fuming nitric acid in a test tube, and largely diluted with water, when oily drops of nitrobenzole are separated; if the liquid be agitated with ether, the nitrobenzole is dissolved, and may be decanted into a fresh tube: to this a mixture of equal parts of alcohol and hydrochloric acid are added, and a few fragments of granulated zinc. The nitrobenzole will thus be reduced to aniline, which may be liberated by the addition of potash in excess: it must be again agitated with ether to dissolve the aniline, and if this ethereal solution be mixed with a solution of chloride of lime, the violet tint characteristic of aniline will be developed.

Dinitrobenzole [$C_{12}H_4(NO_4)_2$].—If benzole be boiled with fuming nitric acid, or if it be allowed to fall, drop by drop, into a mixture of oil of vitriol and nitric acid so long as the liquids mix, dinitrobenzole is formed; the liquid must be boiled for a few minutes, and, on cooling, the dinitrobenzole is deposited in the form of a crystalline magma. It must be washed with water, and recrystallized from alcohol: it melts at a temperature below 212°. Dinitrobenzole represents benzole in which two equivalents of peroxide of nitrogen have taken the place of two equivalents of hydrogen. If its alcoholic solution be treated with hydrosulphate of ammonia, nitraniline (page 258) is produced.

(1321) *Derivatives of Nitrobenzole obtained by reduction.*—Nitrobenzole experiences a reduction of a different kind if it be treated with an alcoholic solution of potash; *azoxibenzide* ($C_{12}H_5NO$) is then formed, and may be obtained by distilling the liquid until it separates into two layers; the upper oily one, when washed with water, yields brown needles of azoxibenzide; they may be purified by dissolving them in alcohol, and transmitting a current of chlorine (to destroy the colouring matter), and recrystallizing. The crystals thus obtained are of a sulphur yellow colour, and often exceed an inch in length. It is fusible at 97°. When distilled it yields aniline, and a new body termed azobenzide.

Azobenzide $(C_{12}H_5N)_2$ may also be procured by distilling nitrobenzide with an alcoholic solution of potash; towards the end of the distillation, it passes over in the form of a red oil, which solidifies in large crystals: it may be purified by re-crystallization from ether, and may be obtained in the form of orange-coloured plates, which are freely soluble in alcohol, but scarcely so in water. It fuses at 149°, and boils at 380°, and may be distilled unaltered. When an alcoholic solution of azobenzide is treated with hydrosulphate of ammonia, or with sulphurous acid, it is converted into a base called *benzidine* ($C_{12}H_6N$). The exact decompositions whi attend the conversion of nitrobenzole successively into azoxibenzide, azobenzide, and benzidine, have not been clearly made out. I azobenzide be treated with nitric acid, it yields two substitutio compounds ($C_{24}H_9(NO_4)N_2$; and $C_{24}H_8(NO_4)_2N_2$)—the latter, whe reduced by hydrosulphate of ammonia, yields another base, terme *diphenine*, which is of a yellow colour; it is soluble in ether:—

$$\overbrace{C_{24}H_8(NO_4)_2N_2}^{\text{Dinitro-azobenzide.}} + 12\,HS = \overbrace{2\,(C_{12}H_6N_2)}^{\text{Diphenine.}} + 8\,HO + 12\,S.$$

(1322) PHENIC, or *Carbolic Acid*; *Hydrate of Phenyl*; *Phen* ($C_{12}H_6O_2 = HO, C_{12}H_5O$) *Sp. gr.* 1·065.—This substance is th most abundant acid product of the distillation of pit-coal. It i also produced by the distillation of the salicylates of the alkali and of the earths (1230). It is likewise found amongst the produc of the distillation of gum benzoin, and of the resin of the *Xa thorrhœa hastilis*. Stædeler has found phenic acid in the urine the cow, and of some other animals.

Laurent obtains phenic acid from the oil of coal-tar, by collecti separately those portions which boil at between 300° and 400°, a mixing with this oil a hot saturated solution of hydrate of potas adding a quantity of the powdered hydrate; a copious separation a white crystalline substance immediately occurs. The still liqu portion must be decanted, and the crystallized matter dissolved a small quantity of water. When thus treated it separates in two layers, the denser of which consists of an aqueous solution phenate of potash. This portion must be separated from t lighter oily layer, and must be neutralized by the addition hydrochloric acid. Carbolic acid rises to the surface. It must digested upon chloride of calcium to remove water, and afterwar distilled, and exposed to a temperature which is gradually lowere It then crystallizes in long colourless needles, which must preserved from contact with the atmosphere.

The crystals of phenic acid melt at a temperature of abo 95°, and the liquid enters into ebullition between 369° and 37 The presence of a minute trace of moisture is sufficient to cau the liquefaction of the crystals. Phenic acid is very sparing soluble in water, but it is dissolved by alcohol, ether, and conce trated acetic acid in all proportions. It has a burning taste, and odour of smoke, resembling that of kreasote. Its vapour strong attacks the skin of the lips, and of the gums. Phenic acid p sesses antiseptic properties similar to those of kreasote: inde much of the commercial kreasote [illegible] solely of phenic ac

Its solutions do not redden litmus paper: a drop of it let fall upon paper produces a transient greasy stain. If a splinter of deal be dipped into a solution of phenic acid, and then into nitric or hydrochloric acid, the wood as it dries becomes blue.

Phenic acid, when heated with ammonia in a sealed tube, becomes partially converted into water and aniline (1064). The acid combines with potash, and forms with it a crystalline compound; though it may be distilled, unchanged, from hydrate of potash, and from quicklime or caustic baryta in excess. Phenates of these bases may be obtained, but they are easily decomposed.

(1323) *Homologues of Phenic Acid.*—Phenic acid is accompanied in coal tar by other homologous bodies which greatly resemble it. By subjecting commercial coal tar kreasote to fractionated distillation, Williamson obtained a liquid which boils at 397°, and which is nearly insoluble in solution of ammonia. Williamson terms it *hydrate of oxide of cresyl* ($HO, C_{14}H_7O$); or it might be termed *kresylic acid.* It is soluble in oil of vitriol, producing a violet colour, and forming a compound acid. This substance is polymeric with anisole (1240) and with benzoic alcohol (1211), and would be the phenic acid of the toluic series. When treated with fuming nitric acid, it is oxidized with almost explosive violence, and a *trinitrokresylic acid* ($HO, C_{14}H_4(NO_4)_3O$), homologous with carbazotic acid, is produced.

It has been suggested that the kreasote of wood tar is a third homologue ($HO, C_{16}H_9O$), in which case it would be the phenic acid of the xylylic series; but the difficulty of purifying kreasote renders its exact composition a matter of uncertainty.

(1324) *Ethers of Phenic Acid.*—Phenic acid may be caused to enter into combination with the oxides of the alcohol radicles by a process of double decomposition, which consists in distilling the sulphomethylate, sulphethylate, or sulphamylate of potash, with phenate of potash. These ethers may also be procured by heating phenate of potash with the iodides of methyl, of ethyl, or of amyl; they are also produced by the distillation of the salicylic ethers with caustic baryta: the preparation of anisole by the latter process being represented by the equation:—

$$\overbrace{C_2H_3O, C_{14}H_5O_5}^{\text{Salicylate of Methyl.}} + 2\,BaO = 2\,(BaO, CO_2) + \overbrace{C_2H_3O, C_{12}H_5O.}^{\text{Phenate of Methyl.}}$$

Anisic acid, which is metameric with salicylate of methyl, also yields phenate of methyl, which is identical with anisole.

The ethers of phenic acid may thus be contrasted with the acid itself:—

		Boiling Point.	Specific Gravity, Liquid.
Phenic, or carbolic acid	$HO,C_{12}H_5O$	370°	1·065
Phenate of methyl, or anisole	$C_2\ H_3\ O,C_{12}H_5O$	306°	0·991
Phenate of ethyl, or phenetole	$C_4\ H_5\ O,C_{12}H_5O$	342°	
Phenate of amyl, phenamylole	$C_{10}H_{11}O,C_{12}H_5O$	437°	

Each of these ethers, when treated with nitric acid, yields substitution compounds analogous to those furnished by anisole (1240), and when submitted to the action of hydrosulphate of ammonia bases are obtained analogous to anisidine, nitranisidine, and dinitranisidine.

(1325) *Products of the Decomposition of Phenic Acid.*—When distilled with perchloride of phosphorus, phenic acid yields *chloride of phenyl* ($C_{12}H_5Cl$), which is a colourless mobile liquid, with a fragrant smell, resembling that of bitter almonds: it boils at 277°. At the same time *phosphate of phenyl* is formed; it may be obtained at a low temperature in beautiful crystals. When melted, it is slightly yellow, and has a fluorescent property. If terchloride of phosphorus be substituted for the perchloride, chloride of phenyl and phosphite of phenyl are produced; and the latter, when distilled, yields benzole, amongst the products (Williamson). Benzole, it will be remarked, contains two equivalents of oxygen less than phenic acid; the phosphorous acid in this case deoxidizes the phenic acid, and becomes converted into phosphoric acid.

Phenic acid gives rise by substitution to an unusual number of acid compounds, formed upon the type of phenic acid itself: such for example as the following:—

Phenic, or carbolic acid	$HO,\ C_{12}H_5,\ O$
Dichlorophenic, or chlorophenesic do.	$HO,\ C_{12}H_3Cl_2,\ O$
Trichlorophenic, or chlorophenisic do.	$HO,\ C_{12}H_2Cl_3.\ O$
Pentachlorophenic, or chlorophenusic do.	$HO,\ C_{12}\quad Cl_5,\ O$
Bromophenic, or bromophenasic do. .	$HO,\ C_{12}H_4Br,\ O$
Dibromophenic, or bromophenesic do.	$HO,\ C_{12}H_3Br_2.O$
Tribromophenic, or bromophenisic do. .	$HO,\ C_{12}H_2Br_3.O$
Nitrophenic, or nitrophenasic acid . .	$HO,\ C_{12}H_4\,(NO_4).O$
Dinitrophenic, or nitrophenesic acid .	$HO,\ C_{12}H_3\,(NO_4)_2.\ O$
Trinitrophenic, or nitrophenisic acid .	$HO,\ C_{12}H_2\,(NO_4)_3.\ O$
Dichloronitrophenic acid	$HO,\ C_{12}H_2Cl_2\,(NO_4).\ O$
Diniodo-nitrophenic acid	$HO,\ C_{12}H_2I_2\,(NO_4),\ O$
Bromodinitrophenic acid	$HO,\ C_{12}H_2Br\,(NO_4)_2,\ O$

All of these acids are monobasic, and form definite salts many of which crystallize very beautifully.

A mixture of chlorate of potash and hydrochloric acid converts phenic acid into trichlorophenic acid ($HO, C_{12}H_2Cl_3O$), and by prolonging the action, chloranil ($C_{12}Cl_4O_4$) is produced.

Oil of vitriol dissolves phenic acid, without change of colour, and produces a compound acid, termed *sulphophenic* acid ($HO, C_{12}H_5O, S_2O_6$); it forms with baryta, a soluble salt, which crystallizes in tufts of needles.

If phenic acid be allowed to fall, drop by drop, into fuming nitric acid, it is attacked with great violence; each drop produces a hissing like that which accompanies the quenching of a hot iron; and upon boiling the mixture, carbazotic (*trinitrophenic*) [$HO, C_{12}H_2(NO_4)_3O$] acid is obtained. If the acid be more dilute, *nitrophenic* acid [$HO, C_{12}H_4(NO_4)O$] or *dinitrophenic* acid [$HO, C_{12}H_3(NO_4)_2O$] is produced. Both of these acids may readily be obtained in crystals: most of their salts crystallize with facility; they greatly resemble the carbazotates.

(1326) CARBAZOTIC, *trinitrophenic*, *nitro-phenisic*, or *picric acid* ($HO, C_{12}H_2 (NO_4)_3O$).—This is a frequent product of the action of nitric acid upon complex organic substances. Phenic acid, salicin, coumarin, phloridzin, silk, indigo, and a variety of resins yield it when treated with fuming nitric acid. The oil of tar, which distils over at a temperature between 300° and 400°, is one of the best raw materials from which this acid can be procured. The resin of the *Xanthorrhœa hastilis* is also a convenient source of carbazotic acid. The hot solution obtained by acting upon these bodies with nitric acid must be decanted from the undissolved portions, and the carbazotic acid, which is deposited as the liquid cools, may be purified by washing with cold water, and converting it into a salt of ammonia or of potash, which may be readily obtained in crystals; the carbazotate of ammonia or of potash when dissolved in boiling water may then be decomposed by dilute nitric acid, and crystals of carbazotic acid will be obtained as the liquid cools.

Carbazotic acid crystallizes in long, pale yellow, brilliant, rectangular plates, which are readily soluble in alcohol and in ether. It requires between 80 and 90 parts of cold water for its solution, forming a liquid of a bright yellow colour, and stains the skin yellow. This acid has an intensely bitter taste, which has induced some persons fraudulently to substitute it in beer for a portion of the hops. Carbazotic acid is also employed for dyeing silk, to which it imparts a beautiful yellow colour, after the silk has been mordanted with alum, or with cream of tartar.

On the application of heat carbazotic acid fuses to a yellowish oil, and if the temperature be gradually raised, it may be partially sublimed, but if suddenly heated it is decomposed with explosion. Concentrated sulphuric and nitric acids dissolve it unaltered, and deposit it on dilution. The carbazotates generally crystallize with facility; they are bitter and of a yellow colour: when heated they are decomposed with explosion. Carbazotate of *potash* is anhydrous; it is freely soluble in boiling water, but requires 260 parts of cold water for solution. The salt of *ammonia* is also anhydrous, but it is more soluble in water, and is somewhat soluble in alcohol. The *soda* salt is readily soluble in cold water. The carbazotates of the alkaline earths, and of lead and silver, are freely soluble.

When the nitrous derivatives of phenic acid are submitted to the reducing action of hydrosulphate of ammonia two red amidated acids are produced. The compound obtained from dinitrophenic acid is termed *nitro-phenamic* acid [$HO, C_{24}H_{11} (NO_4)_2N_2O_3, 4Aq$]; that from carbazotic acid is named *picramic* acid [$HO, C_{12}H_4 (NO_4)_2NO$].

(1327) *Oxyphenic Acid*, or *Pyrocatechin* ($C_{12}H_6O_4$) is a substance which may be noticed in connexion with phenic acid. No direct relation has been traced between these two acids, but the formula of oxyphenic differs from that of phenic acid by two equivalents of oxygen. Oxyphenic acid is obtained most abundantly by the distillation of catechu and of moritannic acid, and of gum-ammoniacum; the acid liquid which passes over during the operation must be decanted from tarry matters which accompany it, and be left to spontaneous evaporation. The crystals which are gradually deposited must be freed from the mother liquor by pressure between folds of filtering paper, and purified by sublimation.

Oxyphenic acid crystallizes in colourless rectangular prisms. It is very soluble in water and in alcohol, but is nearly insoluble in ether. It has a bitter taste, but scarcely any acid reaction. Its crystals fuse between 230° and 240°, and the liquid enters into ebullition between 464° and 473°. Its solutions in the alkalies become first green, then brown, and finally black, whilst oxygen is absorbed. Its most characteristic reaction is the dark green colour which it produces on the addition of perchloride of lime; on the addition of any alkaline solution this colour is changed to a deep red. With acetate of lead it yields a white precipitate. Nitric acid decomposes oxyphenic acid, and oxalic acid is formed.

(1328) *Styphnic Acid* ($C_{12}H_3N_3O_{16}=2HO,C_{12}H(NO_4)_3O_2$).—The omposition of this acid is such that it has been supposed to bear he same relation to oxyphenic acid, that carbazotic acid does to henic acid. This view, however, is not very probable, since the cid is dibasic, and it cannot be obtained from oxyphenic acid by he action of nitric acid upon it. It is the product of the action of nitric acid (sp. gr. 1·20) upon certain gum resins, such as ammoniacum, assafœtida, and sagapenum. The aqueous extracts of Brazil-wood and of the *Morus tinctoria*, also yield it when treated with nitric acid. Many of these substances furnish oxyphenic acid by distillation: extract of Brazil-wood yields it abundantly by this process. Styphnic acid is sparingly soluble in cold water, but readily so in alcohol and in ether. It crystallizes in long prisms, which have a yellow colour. Its solution stains the skin permanently yellow. Styphnic acid reddens litmus, and decomposes the alkaline carbonates with effervescence. It also dissolves metallic iron and zinc with facility. Its taste is somewhat astringent, but not acid. The styphnates, like the carbazotates, are decomposed with explosion, when gently heated. This acid forms two classes of salts, a neutral and an acid one. It appears to be dibasic, and many of its salts crystallize readily.

2. *Naphthalic Series.*

(1329) **Naphthalin** ($C_{20}H_8$). *Sp. gr. of solid* 1·153; *of vapour* 4·528.—This substance derives its principal interest from the important researches to which it was submitted by Laurent, and upon which he principally founded his theory of substitutions. Naphthalin is a constituent of the principal varieties of tar, but it is most abundant in coal tar, particularly in that obtained from the London gas-works. It is also produced when olefiant gas, phenic acid, and some other constituents of coal tar, are transmitted slowly through red-hot tubes. Naphthalin is easily obtained from the last portions of the distillate from tar, which become semisolid on cooling. The liquid constituents of this mass must be separated from it by pressure, and after recrystallization from hot alcohol it may be obtained perfectly pure by sublimation.

Naphthalin forms flaky crystals, consisting of rhombic plates, which have an unctuous feel and a pearly lustre: it has a peculiar odour, and a biting and somewhat aromatic taste. It gradually undergoes sublimation at ordinary temperatures, and is easily distilled over with the vapours of water. It fuses at about 174°, and boils at 428°. Naphthalin does not readily take fire, but when kindled it burns with a white smoky flame. It is insoluble in water, but is readily soluble in alcohol, ether, oil of turpenti and the fixed oils. Potash is without action upon it.

(1330) *Action of Sulphuric Acid upon Naphthalin.*—Sulphu acid when heated with naphthalin combines with it. If th naphthalin be in excess, the acid forms with it a neutral fusibl compound, termed *sulphonaphthalin.* If the sulphuric acid be i excess, and the temperature do not exceed 200°, a semisol acid compound is formed, the *sulphonaphthalic.* If a highe temperature be employed, especially if fuming sulphuric acid b used, *disulphonaphthalic acid* is also formed; it is a brow deliquescent compound, with a sour and bitter taste.

In all these cases the combination of hydrated sulphuric ac with naphthalin is attended with the separation of water; thus:–

Sulpho-naphthalin	$C_{20}H_7SO_2 =$ $C_{20}H_8 + HO, SO_3 - 2\ HO$
Sulpho-naphthalic, termed also hypo-sulpho-naphthalic acid . . .	$HO, C_{20}H_7S_2O_5 =$ $C_{20}H_8 + 2\ (HO, SO_3) - 2\ HO$
Disulpho-naphthalic acid, (thio-naphtic, or hyposulpho-naphtinic acid) .	$2\ HO, C_{20}H_6S_4O_{10} =$ $C_{20}H_8 + 4\ (HO, SO_3) - 4\ HO$

Besides these two acids, a small quantity of a third acid is sometimes obtained, which is metameric with the sulpho-naphthalic; from the latter, this new acid is distinguished by the difference in th effect of heat upon its baryta salt, which when burned in open a smoulders like tinder till the naphthalin is consumed, whilst th sulpho-naphthalate of baryta burns with a luminous flame. Th sulpho-naphthalates are soluble in water, and many of them i alcohol also; they have a bitter, almost metallic, taste.

(1331) *Action of Nitric Acid upon Naphthalin.*—Nitric aci attacks naphthalin slowly at ordinary temperatures, and converts it into a sulphur-yellow compound, termed *nitro-naphthali* [$C_{20}H_7(NO_4)$]; at higher temperatures *dinitro-naphthalin* [$C_{20}H_6$ $(NO_4)_2$] and *trinitro-naphthalin* [$C_{20}H_5(NO_4)_3$] are produced. These different varieties of nitro-naphthalin crystallize beautifully from their alcoholic or their ethereal solutions. When solutions of these compounds are exposed to the reducing action o hydrosulphate of ammonia, each compound yields an azotised base; *naphthalidine,* or *naphthylamine* ($C_{20}H_9N$) being that furnished from nitro-naphthalin, and *semi-napthalidam* ($C_{20}H_{10}N_2$) from dinitro-naphthalin; and a third base was obtained by Lauren from trinitro-naphthalin. By prolonged boiling with nitric acid naphthalin is converted into a mixture of oxalic and phthalicacids:–

$$\overbrace{C_{20}H_8}^{\text{Naphthalin.}} + 16\ O = \overbrace{2\ HO, C_{16}H_4O_6}^{\text{Phthalic Acid.}} + \overbrace{2\ HO, C_4O_6}^{\text{Oxalic Acid.}}.$$

Phthalic, or *Naphthalic Acid* ($2\,HO, C_{16}H_4O_6$), is produced by the long-continued action of nitric acid upon naphthalin, as well as upon the bichloride of naphthalin, and upon alizarin. The atter mode of its production is interesting, since it indicates a connexion between naphthalin and the colouring matter of madder. On evaporating the solution obtained by acting upon naphthalin with boiling nitric acid, phthalic acid is deposited in groups of lamellar crystals. It is sparingly soluble in cold water, and very soluble in alcohol and in ether. When exposed to a high temperature, water is expelled, and phthalic anhydride is sublimed. By still further prolonging the action of nitric upon phthalic acid, a *nitrophthalic* acid [$2HO, C_{16}H_3(NO_4)O_6$] may be procured. If phthalic acid be distilled with lime, carbonate of lime and benzole are the results:—

$$\overbrace{2\,HO, C_{16}H_4O_6}^{\text{Phthalic Acid.}} + 4\,CaO = 4\,(CaO, CO_2) + \overbrace{C_{12}H_6}^{\text{Benzole.}}.$$

Phthalic acid is dibasic, and Hofmann has suggested that it may form one member of a series of acids which would bear the same relation to the monobasic aromatic acids as the dibasic acids of the oxalic series bear to the volatile fatty acids; and he has obtained from cuminic acid, by the oxidizing influence of nitric acid upon it, a compound which, from its sparing solubility, he has termed *insolinic acid*. This acid is also dibasic. The two classes of acids would be represented thus—insolinic acid having, as yet, no representative in the monobasic series:—

Aromatic Monobasic Acids. $HO, C_nH_{n-9}O_3$.		Corresponding Dibasic Acids, $2\,HO, C_nH_{n-12}O_6$.	
Benzoic . . .	$HO, C_{14}H_5\,O_3$	. . . .	?
Toluic . . .	$HO, C_{16}H_7\,O_3$	Phthalic . .	$2\,HO, C_{16}H_4O_6$
. . . .	?	Insolinic . .	$2\,HO, C_{18}H_6O_6$
. . . .	?	. . . .	?
Cuminic . . .	$HO, C_{20}H_{11}O_3$	. . . .	?

(1332) *Action of Chlorine on Naphthalin.*—When chlorine is brought into contact with naphthalin, the two bodies enter into direct combination: the naphthalin fuses, and a mixture of two compounds, presenting considerable analogy to Dutch liquid, is formed. One of these compounds has been termed, somewhat inappropriately, *chloride of naphthalin* ($C_{20}H_8Cl_2 = C_{20}H_7Cl, HCl$), and the other, *bichloride of naphthalin* ($C_{20}H_8Cl_4 = C_{20}H_6Cl_2, 2\,HCl$). The formation of small quantities of substitution derivatives of naphthalin also usually accompanies the production of these compounds. It would have been more correct to have termed the first, *hydrochlorate of chlonaphtase*, and the second, *bihydrochlorate of chlonaphtese*. To avoid confusion, we shall, however, retain the terms of chloride and bichloride of naphthalin.

Chloride of Naphthalin ($C_{20}H_8Cl_2$) is an oily body, which is soluble in ether in all proportions. This circumstance is taken advantage of in effecting its partial separation from the bichloride, which is solid; but it is difficult to free it completely from this latter substance. *Bichloride of naphthalin* ($C_{20}H_8Cl_4$) exists in two modifications, which have been distinguished by the letters *α* and *β*. These modifications are both formed simultaneously during the action of chlorine upon naphthalin. The *bichloride α* is sparingly soluble in boiling ether, from which, on cooling, it is deposited in crystals; or it may be purified still more advantageously by crystallization from boiling oil of petroleum. It is scarcely soluble in alcohol. The *bichloride β* is very soluble in alcohol, and still more so in ether. It is obtained by exposing the ethereal mother-liquor, from which the bichloride *α* has crystallized, to a low temperature for a few hours, and recrystallizing the deposit (which consists of a mixture of the modifications of *α* and *β*) from ether the liquid retains the modification *β*, which must be recrystallized until the crystals obtained are rapidly dissolved by cold ether Corresponding compounds with bromine may be obtained, and other derivatives also may be formed, into the composition of which both chlorine and bromine enter. (See Table 1, page 577.)

Both the liquid chloride and the two modifications of the bichloride of naphthalin are decomposed by distillation. When treated with an alcoholic solution of potash, they are decomposed chloride of potassium is formed, and chlorinated derivatives of naphthalin are produced. In these new compounds the number of equivalents of chlorine and hydrogen together is always equal to 8, which is the number of equivalents of hydrogen in naphthalin.

The researches of Laurent have disclosed the existence of an exceedingly numerous series of substitution compounds, formed upon the type of naphthalin, into the composition of which chlorine enters.

Corresponding compounds with bromine may also be formed and another series may be obtained, in which the substitution is effected partly by chlorine and partly by bromine. It would be inconsistent with the plan of the present work to attempt to give any detailed account of these bodies. The table which follows will indicate the composition of the principal compounds of this series. These bodies are of little practical importance, but their investigation led Laurent to theoretical deductions regarding the molecular constitution of chemical compounds generally, which have exerted a remarkable influence upon the recent progress of organic chemistry.*

1. *Chlorides and Bromides of Naphthalin.*

	1.	2.
Liquid chloride of naphthalin .	$C_{20}H_8, Cl_2$	$C_{20}H_7Cl, HCl$
Chloride of bronaphtase . .	$C_{20}H_7Br, Cl_2$	$C_{20}H_6BrCl, HCl$
Bichloride of naphthalin . .	$C_{20}H_8, Cl_4$	$C_{20}H_6Cl_2, 2\ HCl$
Bichloride of chlonaphtase .	$C_{20}H_7Cl, Cl_4$	$C_{20}H_5Cl_3, 2\ HCl$
Bichlorobromide of naphthalin .	$C_{20}H_8, Cl_3Br$	$C_{20}H_6Cl_2, HCl, HBr$
Bichloride of chlonaphtese .	$C_{20}H_6Cl_2, Cl_4$	$C_{20}H_4Cl_4, 2\ HCl$
Bichloride of bronaphtese .	$C_{20}H_6Br_2, Cl_4$	$C_{20}H_4Cl_2Br_2, 2\ HCl$
Bibromide of chlonaphtese .	$C_{20}H_6Cl_2, Br_4$	$C_{20}H_4Cl_2Br_2, 2\ HBr$
Bibromide of chlorabronaphtese	$C_{20}H_6ClBr, Br_4$	$C_{20}H_4Cl\ Br_3, 2\ HBr$
Bibromide of bronaphtese .	$C_{20}H_6Br_2, Br_4$	$C_{20}H_4Br_4, 2\ HBr$
Bibromide of bromechlonaphtise	$C_{20}H_5Br_2Cl, Br_4$	$C_{20}H_3Br_4Cl, 2\ HBr$
Bibromide of bronaphtise . .	$C_{20}H_5Br_3, Br_4$	$C_{20}H_3Br_5, 2\ HBr$

Many of these compounds are isomorphous.

The compounds which are contained in the foregoing table are susceptible of decomposition by means of an alcoholic solution of potash, which effects the removal of a certain portion of chlorine or of bromine, and the compound which is left is one of those represented in the following table:—

2. *Compounds formed upon the type* ($C_{20}H_8$).

Chlonaphtase .	$C_{20}H_7Cl$	Chlonaphtose . .	$C_{20}H_4Cl_4$
Bronaphtase .	$C_{20}H_7Br$	Chlorebronaphtose .	$C_{20}H_4Cl_2Br_2$
Chlonaphtese .	$C_{20}H_6Cl_2$	Chloribronaphtose .	$C_{20}H_4Cl_3Br$
Bronaphtese .	$C_{20}H_6Br_2$	Bronaphtose . .	$C_{20}H_4Br_4$
Chlonaphtise .	$C_{20}H_5Cl_3$	Bromechlonaphtuse .	$C_{20}H_3Br_2Cl_3$
Bronaphtise .	$C_{20}H_5Br_3$	Chlonaphthalase .	$C_{20}H_2Cl_6$
Chlorebronaphtise	$C_{20}H_5Cl_2Br$	Chlonaphthalise .	$C_{20}\ \ Cl_8$

From the results of this decomposition it appears probable that the formulæ given in the third column of the first table represent, more accurately than those of the second column, the true composition of the so-called chlorides and bromides of naphthal the names of which would require modification accordingly.

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* The names proposed by Laurent, extraordinary and uncouth as many of them appear, are yet well adapted to represent the numerous substitution compounds to which they refer. In the case of naphthalin, the compounds which contain chlorine are indicated by the prefix *chlo*, and end with a syllable in which the vowels *a*, *e*, *i*, *o*, and *u*, are intended respectively to indicate the displacement of 1, 2, 3, 4, or 5 equivalents of hydrogen. In *chlo*naphta*se* 1 equivalent of hydrogen has been displaced by 1 equivalent of chlorine; in chlonapht*ose*, 4 equivalents of hydrogen have been displaced by 4 of chlorine. If the number of equivalents of hydrogen exceed 5, a fresh syllable, such as *al*, is added to the word, and the vowels (beginning with *a*) are again employed

It must not, however, be supposed that the foregoing ta indicate all the combinations of chlorine with naphthalin, wh may be formed by substitution or otherwise. Many of these d ferent compounds exist in several distinct modifications. The are, for example, no fewer than seven distinct forms of *chlonaph tese*, which Laurent has distinguished by the letters *a*, *c*, *ad*, *f*, *x*, and *y*; four of them, *a*, *c*, *f*, and *x*, are obtained by the dis tillation of the bichloride of naphthalin, and two of them, a and *e*, by treating the same compound with potash, and *y* is the result of the action of chlorine upon dinitronaphthalin.

a and *x* are liquid at ordinary temperatures, *c* crystallizes i needles, which fuse at 122°, *f* crystallizes in tables, fusible at 1 *ad* crystallizes in needles, which fuse at about 85°, *e* fuses at *y* fuses at 203°, and may be sublimed in plates. Many of these bodies are also distinguished by differences in the degree of their solubility in alcohol and in ether, and by the different way i which they are attacked by chlorine and by bromine.

The existence of these remarkable modifications of chlonaphtese was accounted for by Laurent, on the supposition that in the compound ($C_{20}H_8$), or naphthalin, each of the 8 equivalents or atoms of hydrogen had its distinct or allotted position in the compound molecule. In chlonaphtese 2 of these molecules of hydrogen are displaced by 2 equivalents of chlorine, but it is not a matter of indifference which of the molecules are thus displaced. Thus, if $\left\{C_{20}\begin{matrix}1. & 2. & 3. & 4.\\ 5. & 6. & 7. & 8.\end{matrix}\right\}$ represent the compound molecule of naphthalin, each figure indicating a distinct molecule of hydrogen, it is not a matter of indifference whether the displacement shall take place thus,

$$\left\{C_{20}\begin{matrix}1, & 2, & 3, & 4\\ 5, & 6, & Cl, & Cl\end{matrix}\right\} \text{ or thus } \left\{C_{20}\begin{matrix}1, & 2, & Cl, & Cl\\ 5, & 6, & 7, & 8\end{matrix}\right\} \text{ or thus } \left\{C_{20}\begin{matrix}1, & 2, & 3, & Cl\\ 5, & 6, & 7, & Cl\end{matrix}\right\}.$$

In all these cases we should still have compounds which on analysis would exhibit a perfectly similar composition; and yet

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as before. Thus to express the substitution of 6 equivalents of hydrogen b 6 of chlorine, the term chlonaphth*alase* is adopted. If bromine be the displacing body, the prefix *bro* is employed, and if both chlorine and bromi be present, the name employed indicates by the vowel in the concludi syllable the total number of equivalents of hydrogen displaced, whilst th number of one of the halogens is indicated by a vowel attached to the pref of the particular halogen to be represented. Thus *chloribronaphtose* indicat (C_{20}, H_4Cl_3Br), or a compound in which 4 equivalents of hydrogen have be displaced by 3 equivalents of chlorine, and by one of bromine: the nam *bromechlonaphtose* indicates that the 4 equ [illegible] hydrogen displaced a represented by 2 equivalents of bro [illegible] ine.

from the different relative position of the atoms of chlorine in the compound, the properties of each might be different. It may be shown by calculation, upon the principle of permutation, that twenty-eight such varieties of chlonaphtese are possible; of these seven have been discovered. This subject is placed in a very clear light by Gregory; (see also p. 202).

Chlonaphtise may also be obtained in seven different forms, all of which are crystallizable solids. *Chlonaphtose* is known under four different modifications. The compounds which contain both chlorine and bromine of the type *naphtose,* in which 4 equivalents of hydrogen have been displaced, may be formed in three different ways, and yield three metameric modifications, viz.:—1. *Chloribronaphtose,* which is obtained by exposing a mixture of bromine and chlonaphtise to the sun's rays; it forms six-sided prisms, which are fusible, and solidify at a temperature of about 221°. 2. *Bromachlonaphtose a,* which is obtained by passing a current of chlorine over heated bronaphtese: it forms six-sided prisms of the consistence of wax, which after fusion solidify at 230°. 3. *Bromachlonaphtose* β, which is obtained by the distillation of bichloride of bronaphtese; it forms flattened oblique prisms. Various modifications of many of the other chlorides might be enumerated, but it is unnecessary to particularize further. This great variety of form admits of explanation upon the hypothesis already applied to account for the different forms of chlonaphtese. It is obvious that numerous as are the modifications of many of the forms of these derivatives of naphthalin, they constitute but a small number of the possible varieties which a permutation in the relative position of the elementary atoms of the compound would permit.

(1333) *Paranaphthalin, or Anthracene* ($C_{30}H_{12}$?). *Sp. gr. of vapour* 6·741.—This substance accompanies naphthalin in the last stages of the distillation of coal tar. It may be purified from naphthalin by means of alcohol, which dissolves the naphthalin, but leaves almost all the paranaphthalin untouched. Paranaphthalin is polymeric with naphthalin; it is a white solid, which fuses at 356°, and boils at a temperature above 572°. It may be distilled without being decomposed, and it condenses in lamellar crystals. Its best solvent is oil of turpentine. Chlorine acts slowly upon paranaphthalin, forming a compound, which has the composition represented by $C_{30}H_{10}Cl_2$, hydrochloric acid being eliminated during its formation. A corresponding compound, containing peroxide of nitrogen, may also be obtained.

(1334) *Metanaphthalin* (the *retisterene* of Dumas) is anoth compound polymeric with naphthalin: it was obtained by Pelle and Walter during the distillation of rosin. This body is sparing soluble in cold alcohol, but is readily dissolved by boiling alcoh as well as by ether, naphtha, and oil of turpentine. It fuses 153°, and boils at 617°. It does not appear to form any comp acid when treated with oil of vitriol.

(1335) During the distillation of the bituminous shale Dorsetshire various products are obtained, which greatly resem those contained in coal tar. The hydrocarbons approach in com-position to $(C_2H)_n$. A portion of the oil, which boils betwe 390° and 480°, furnishes a substance resembling kreasote, whi Laurent termed *ampelin:* it is soluble to a considerable exte in water, but the addition of a few drops of an acid or of th solution of certain salts causes the separation of the ampeli Ampelin is decomposed when the attempt to redistil it is made. B treating the oils of schist with nitric acid, Laurent obtained a acid metameric with the salicylic, and which he termed *ampelic* aci

Shale tar is particularly rich in basic substances. G. Willia has detected in it, in addition to Runge's pyrrol bases (1067 ammonia, pyridine, picoline, lutidine, collidine, and parvoline besides two other bases as yet but imperfectly examined, whic have been termed *carmidine* and *vertidine*. It is remarkable tha aniline is not present amongst these bases. (*Q. J. Chem. Soc.*, vii., 97

The destructive distillation of bones, and of azotised anima matters generally, yields a substance commonly known as *Dippel's* *animal oil.* This oil comes over accompanied by an aqueou liquid, charged with carbonate, hydrosulphate, and hydrocyanate of ammonia. The oil itself is a complex mixture, consisting of a part which is soluble in acids, and of an insoluble portion; the latter constituting the larger part of the oil. In the portion soluble in acids various volatile bases are present, including methylia, ethylia, tritylia, and tetrylia,—aniline, pyridine, picoline, lutidine,—and the pyrrol bases. The portion insoluble in acids contains benzole, and a mixture of several nitriles.

(1336) *Bitumen, Asphalt, and Petroleum.*—Closely connected with the products of destructive distillation are the different forms of bitumen, asphalt, and petroleum. Deposits of these substances are found in various localities, as, for example, at Trinidad, at Amiano and in some other parts of the north of Italy, and also on the borders of the Caspian Sea, where it occurs in beds of marl above coal measures. It is also abundant at Rangoon, and in several other localities of the kingdom of Burmah, where e naphtha is obtained from a pale blue clay, soaked with oil, hich rests upon roofing slate, beneath which is coal containing uch pyrites. The *petroleum* from the last named locality has ecently been made the subject of examination by De La Rue and I. Müller. (*Proceed. Roy. Soc.*, viii. 221.) It is obtained by inking wells about sixty feet deep, in which the liquid is collected s it oozes from the soil. At common temperatures it has the onsistence of goose-fat; it is lighter than water, and has usually a reenish-brown colour; it has also a slight, peculiar, but not unleasant odour. It is composed almost entirely of volatile constituents; the fixed residue not amounting to more than 4 per cent. if it be distilled in a current of superheated steam. About 10 or 11 per cent. of the volatile matters consists of a body which is solid at ordinary temperatures (paraffin). When the liquid portion is agitated with oil of vitriol, some of its constituents enter into combination with the acid, but the greater part remains unaltered by this agent. In the portion which combines with the acid, benzole, toluole, xylole, and cumole, have been identified, and there are several basic substances which have not as yet been completely examined. The liquid from which the hydrocarbons of the benzole series have been removed by the action of oil of vitriol, after being rectified, constitutes *rock oil* or *naphtha*; it is a mixture of several hydrocarbons; it is the liquid in which potassium and sodium are preserved. In order to purify it for this purpose, the crude distillate must be agitated several times with a fifth of its bulk of oil of vitriol; after which the undecomposed hydrocarbon is to be well washed with water, and rectified from quicklime. This liquid requires about eight times its bulk of alcohol for solution, but it is soluble in all proportions in ether and in the volatile oils. Hot naphtha dissolves phosphorus and sulphur, but deposits the greater portion of these bodies on cooling. It also dissolves caoutchouc, camphor, and fatty and resinous bodies generally. Pelletier and Walter describe three components of naphtha; one, which is termed *naphtha*, boils at about 190°; the second, termed *naphthene* ($C_{16}H_{16}$), boils at 239°; and the third, *naphthole*, at 374°. It is not improbable that all these bodies are polymeric multiples of the hydrocarbon CH.

Asphalt is the term given to solid bitumen (951). The bitumens differ in the facility with which they are attacked by solvents. Generally they contain but little of any matter soluble in alcohol, but most of them are dissolved in great part by ether, and by oil of turpentine. When distilled they yield substances which resemble the paraffin oils in properties and consistence (1307).

CHAPTER X.

DERIVATIVES OF CYANOGEN—UREA—ORGANIC BASES OF ANIM ORIGIN—URIC ACID, PRODUCTS OF ITS DECOMPOSITION.

§ I. DERIVATIVES OF CYANOGEN.

(1337) In describing some of the compounds of cyanogen (allusion was made to some important derivatives of this body taining iron, cobalt, platinum, sulphur, and some other elem which perform the functions of salt-radicles, or bodies which their mode of combination present a certain analogy with halogens. In the present chapter some of these compounds wil described; urea and some organic bases of animal origin will be examined, after which uric acid and its more important vatives will be considered.

(1338) Hydrocyanic acid in its anhydrous form combines several of the anhydrous electro-negative chlorides, such as chloride of iron, bichloride of tin, bichloride of titanium, and chloride of antimony, and forms compounds, the composition which is represented by the formulæ ($2HCy, Fe_2Cl_3$); ($HCy, SnCl$ ($HCy, TiCl_2$); and ($3\,HCy, SbCl_5$); but these compounds are decomposed by water, and have no practical applications.

The general properties of the cyanides have been already cussed; some of these salts are of considerable practical imp tance, and may be now briefly described.

(1339) *Cyanide of Potassium* (KCy).—This salt is prepare in considerable quantities for the purpose of dissolving the salts gold and of silver in the processes of electrotyping; it is also e ployed in photography. It may be obtained by heating to d redness, in a covered iron crucible, a mixture of 8 parts of a hydrous ferrocyanide of potassium, and 3 of dried carbonate potash, until the fused mass has lost its yellow colour, and cea to give off bubbles of gas. The iron is separated in the form a metallic powder, and subsides to the bottom of the crucibl the fused cyanide can then be poured off, and solidifies on cooli to a milk-white mass. The cyanide thus obtained is, howev always mixed with a portion of cyanate, the reaction being su as is shown in the following equation:—

$$2(K_2, FeCy_3) + 2(KO, CO_2) = 5\,KCy + KO,CyO + Fe_2 + 2\,C$$

If the presence of the cyanate of potash be injurious, it may t rid of by adding to the mixture of the carbonate and ferro-anide, before fusion, one-eighth of its weight of charcoal, which a red-heat reduces the cyanate of potash to the form of cyanide. he fused salt, when decanted from the iron, has a black colour, wing to the presence of particles of unconsumed charcoal. If it to be used in solution immediately, it may be dissolved in water nd filtered; but if required in the solid form it may be purified y treatment with boiling alcohol, from which, after filtration, it rystallizes on cooling. Cyanide of potassium forms colourless ubes; it is deliquescent, has an alkaline reaction, and when moist mits an odour of hydrocyanic acid. It is highly poisonous.

Cyanide of potassium is a powerful and valuable reducing agent. The oxides of a large number of metals, including those of lead, copper, and iron, when thrown into the melted salt, are immediately reduced to the metallic state, whilst cyanate of potash is formed. It may also be used in the laboratory as a reducing agent, instead of black flux, in testing for arsenic (718). Solutions of cyanide of potassium dissolve iron, zinc, nickel, and copper, with evolution of hydrogen, whilst potash is produced. Silver and gold are also dissolved by the solution of cyanide of potassium, if air be allowed free access, and double cyanides of potassium with those metals are formed.

(1340) *Double Cyanides.*—Cyanide of potassium, when mixed with metallic solutions, occasions a large number of precipitates, which, in the majority of instances, are soluble in an excess of the cyanide of potassium. The cyanides of the metals of the alkalies and of the alkaline earths may be substituted for cyanide of potassium, and produce similar double cyanides. The double cyanides which are formed in these cases are of two kinds or classes. The double salts of the first class are comparatively unstable, and are decomposed by the addition of a diluted free acid, such as the hydrochloric. In such cases the cyanide of potassium is decomposed, hydrocyanic acid is liberated, and the insoluble metallic cyanide is precipitated. The double salts which the cyanides of zinc, nickel, manganese, copper, and silver form with cyanide of potassium belong to this class. When, for example, the double cyanide of nickel and potassium is decomposed by hydrochloric acid, the following reaction occurs, and cyanide of nickel is precipitated, since it is insoluble either in hydrocyanic or in hydrochloric acid:—

$$\mathrm{NiCy, KCy + HCl = NiCy + KCl + HCy.}$$

The alkalies do not occasion precipitates in the solutions of the double cyanides. The cyanides of this class are highly poisonous.

combines with the cyanogen, and carries it off in the form of hydrocyanic acid, which is arrested by causing it to pass through a solution of nitrate of silver. The cyanide of silver is afterwards collected upon a filter and weighed.

(*a*) *Cyanides which do not form Electro-negative Double Cyanides.*

(1341) The following are some of the principal insoluble metallic cyanides which yield double cyanides of the first class, *i. e.*, double salts, which are decomposed, and yield a precipitate on the addition of a dilute acid.

Cyanide of zinc is white and insoluble in water; with cyanide of potassium it forms a soluble salt (ZnCy, KCy), which may be obtained in large regular anhydrous colourless octohedra. *Cyanide of zinc and sodium* (2 ZnCy, NaCy, 5 Aq) may be obtained in brilliant plates, if cyanide of sodium be substituted for cyanide of potassium. *Cyanide of nickel* (NiCy) forms an apple-green precipitate, which is very soluble in cyanide of potassium, forming a salt (NiCy, KCy, Aq), which crystallizes in oblique rhomboidal prisms of a yellow colour. *Cyanide of manganese* falls as a bulky reddish-white precipitate, on mixing a solution of any salt of manganese with one of cyanide of potassium; it rapidly becomes brown by exposure to the air. This cyanide is soluble in excess of cyanide of potassium, but the solution absorbs oxygen, and gradually deposits oxide of manganese. *Subcyanide of copper*, Cu_2Cy, is a white powder obtained by treating an acid solution of subchloride of copper with cyanide of potassium; it is soluble in the dilute acids. Sulphate of copper yields with cyanide of potassium a brownish-yellow precipitate (CuCy), which soon begins to give off cyanogen, and becomes converted into a double cyanide (Cu_2Cy, CuCy, 5 Aq). The same salt may be obtained in bright green crystals by adding hydrocyanic acid to a solution of sulphate of copper. Cyanide of copper (CuCy) is soluble in excess of cyanide of potassium, with which it forms two salts, (CuCy, KCy) and (CuCy, 3 KCy). The latter is the more soluble salt of the two.

(1342) *Cyanide of silver* (AgCy) is precipitated in dense white flocculi when hydrocyanic acid or cyanide of potassium is added to a solution of nitrate of silver. It is nearly insoluble in dilute nitric acid even at a boiling temperature, but it is soluble in ammonia. When heated gently it melts, and at a high temperature gives off cyanogen, leaving a residue of a grey colour, which retains a portion of cyanogen. Cyanide of silver is freely soluble in solutions of the cyanides of potassium, sodium, barium, calcium, and strontium. These solutions give no precipitate with sol of the metallic chlorides; indeed, cyanide of silver is diss boiling solutions of the chlorides of the metals of the alkalies of the earths. It is also soluble in a solution of nitrate of as well as in solutions of the ferrocyanide and ferridcyan potassium. When ferrocyanide of potassium is used as the vent, a dirty blue precipitate of cyanide of iron is formed, liquid becomes strongly alkaline; $K_2FeCy_3 + 2\,AgCy = FeC$ $2\,(AgCy, KCy)$. The *cyanide of silver and potassium* (Ag KCy) is anhydrous, and may be obtained in octohedra or sided plates. Occasionally it forms rhomboidal prisms with This salt is freely soluble in water and in boiling alcohol. extensively employed for electro-silvering, since its solution mixed with an excess of cyanide of potassium, and then sub to electrolysis, deposits silver in compact coherent plates (87

(1343) *Cyanide of Mercury* (sometimes called *Bicyan Mercury*) (HgCy).—This salt may be prepared either by diss the red oxide of mercury in dilute hydrocyanic acid, in which oxide is soluble with great facility, or by boiling a mixtu 4 parts of finely-powdered Prussian blue and 3 of red oxi mercury, also finely levigated, with 40 parts of water, until undissolved portion has acquired a full brown colour: the filt on evaporation yields the cyanide of mercury. It may also procured by boiling 2 parts of sulphate of mercury with ferrocyanide of potassium and 8 of water:—

$$(K_2FeCy_3) + 3(HgO,SO_3) = 3(HgCy) + 2\,(KO,\ SO_3) + FeO,S$$

Cyanide of mercury crystallizes in anhydrous rectangular pri which are colourless and transparent. It has a nauseous, met taste, and is very poisonous. It requires about 8 parts of cold w for solution; it is less soluble in ordinary alcohol, and nearly i luble in absolute alcohol. Cyanide of mercury is decomposed heated; if perfectly dry it yields cyanogen gas, metallic merc and a residue of paracyanogen. If moist, carbonic acid, amm and hydrocyanic acid are produced.

Cyanide of mercury dissolves the red oxide of mercury fr and forms an oxycyanide (HgO, HgCy); it crystallizes in nee it is sparingly soluble in cold water, and the liquid has an line reaction. Cyanide of mercury does not give any precip of oxide of mercury on the addition of a free alkali. When h with sulphuric or hydrochloric acid it is decomposed, and giv hydrocyanic acid. It is also decomposed by sulphuretted hydr

Cyanide of mercury enters into combination with a great number of chlorides, iodides, bromides, and cyanides, forming with them crystallizable double salts. It does not occasion precipitates when mixed with the solutions of salts of zinc, cobalt, nickel, manganese, and other metals which yield cyanides insoluble in water, with the exception of the salts of palladium; from which it would appear that mercury has a stronger affinity for cyanogen than any of the metals, excepting palladium.

(1344) *Cyanide of Gold.*—The protocyanide (AuCy) is the only cyanide of gold which is accurately known. It may be obtained by several methods; the simplest consists in adding a solution of cyanide of potassium to a dilute solution of terchloride of gold, so long as a precipitate is occasioned. It is a lemon yellow powder, composed of microscopic hexagonal plates. It is decomposed by heat into cyanogen and metallic gold: boiling nitric, sulphuric, and hydrochloric acids do not decompose it, and aqua regia acts upon it very slowly. It is soluble in hyposulphite of soda and in hydrosulphate of ammonia; but its most important solvent is cyanide of potassium, with which it forms a double salt (AuCy, KCy): this compound crystallizes in colourless rhombic octohedra, or in pearly scales. It may be obtained by dissolving either the cyanide of gold or the oxide of gold (precipitated from the terchloride by ammonia) in a solution of cyanide of potassium. Cyanide of gold is also soluble in a solution of the ferrocyanide of potassium. The double cyanide is likewise formed by dissolving finely divided metallic gold in a solution of cyanide of potassium when exposed to the air. The double cyanide of gold and potassium is largely used for gilding by means of the galvanic battery (878).* Copper and silver articles may also be gilt by it without the aid of the battery, by mere immersion; portions of copper or of silver being dissolved during the operation.

(1345) *Cyanide of Palladium* (PdCy).—Palladium has a very powerful affinity for cyanogen; when a solution of a salt of palladium is mixed with one of cyanide of mercury, a yellowish-white precipitate of cyanide of palladium is formed; this precipitate may be dissolved by means of cyanide of potassium, with which it forms a

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* Böttger recovers the gold from the spent gilding solutions by evaporating them to dryness, mixing the residue with its own weight of finely powdered litharge, and fusing the mass; the lead and the gold are reduced, and form a metallic button, which, when treated with nitric acid, leaves the gold in the form of a fine powder.

Ferrocyanogen (hypothetical).	FeC_6N_3.	Fcy.
Hydro-ferrocyanic acid .	$H_2C_6N_3Fe$	H_2, Fcy
Ferrocyanide of potassium .	$K_2C_6N_3Fe$, 3 HO	K_2, Fcy, 3 Aq
Ferrocyanide of sodium .	$Na_2C_6N_3Fe$, 12 Aq	Na_2, Fcy, 12 Aq
Everitt's white salt, or ferrocyanide of potassium and iron . . .	K C_6 N_3Fe_2, or $K_2C_{12}N_6Fe_4$	KFe, Fcy, or K_2Fcy, 3 FeCy
Ordinary Prussian blue .	$C_{18}N_9Fe_7$, 18 HO	Fe_4Fcy_3, 18 Aq
Basic Prussian blue . .	$C_{18}N_9Fe_9O_3$, xHO	Fe_4Fcy_3, Fe_2O_3, xAq
Ferrocyanide of potassium and barium . . .	KBa C_6N_3Fe, 3 HO	KBa, Fcy, 3 Aq
Ferrocyanide of copper .	$Cu_2C_6N_3Fe$, xHO	Cu_2, Fcy, xAq
Ferrocyanide of potassium and copper	KCu C_6N_3Fe, 2 HO	KCu, Fcy, 2 Aq
Ferrocyanide of lead . .	$Pb_2C_6N_3Fe$, 3 HO	Pb_2, Fcy, 3 Aq

(1348) *Hydro-ferrocyanic acid* (H_2FeCy_3).—This compound was originally obtained by Porrett, by the decomposition of ferrocyanide of potassium, by means of tartaric acid. A better plan consists in forming a concentrated aqueous solution of the ferrocyanide, boiling it to expel the air, and then allowing it to cool in a vessel provided with a good cork to exclude air. Ether is then added, and an excess of hydrochloric acid, which has also been deprived of air by boiling. On agitating the mixture, chloride of potassium is formed and remains in solution, and white scales of hydro-ferrocyanic acid are deposited; K_2, $FeCy_3 + 2\ HCl = H_2FeCy_3 + 2\ KCl$. These crystals must be washed with a mixture of alcohol and ether, and dried *in vacuo* over sulphuric acid. Liebig adds by degrees to a cold saturated solution of ferrocyanide of potassium, an equal volume of hydrochloric acid; the white precipitate of hydro-ferrocyanic acid thus obtained must be washed with hydrochloric acid, dried in vacuo upon a tile, and caused to crystallize from its solution in alcohol by the addition of ether.

Hydro-ferrocyanic acid is dibasic. When exposed to the air, it absorbs oxygen and becomes blue: its solution, when boiled, evolves hydrocyanic acid and deposits a white insoluble matter containing both iron and cyanogen. This body becomes blue in the air. It is probably a protocyanide of iron, and by exposure to air it absorbs oxygen, becoming converted into basic Prussian blue, which is a compound of sesquioxide of iron and of true Prussian blue; $9\ FeCy + 3\ O = (Fe_7Cy_9 + Fe_2O_3)$.

(1349) *Ferrocyanide of Potassium*, or *Prussiate of Potash* (K_2, $FeCy_3$, 3 Aq).—This important salt is met with in commerce nearly in a state of purity. It is formed when azotised matters are aqueous solution causes the separation of a portion of the salt in crystalline flakes. Ferrocyanide of potassium is not poisonous; it has a saline bitterish taste. When heated to 212° it loses the whole of its water of crystallization, and crumbles to a yellowish-white powder. When heated to redness in closed vessels it fuses, and at full and prolonged red heat undergoes partial decomposition, nitrogen being evolved, whilst cyanide of potassium and carbide of iron are formed. When heated with peroxide of manganese, cyanate of potash is formed (411).

Ferrocyanide of potassium, when distilled with sulphuric acid, furnishes abundance of hydrocyanic acid; the decomposition which attends the reaction has been already explained (*note*, § 408). When heated with concentrated oil of vitriol, the salt is decomposed into carbonic oxide, and a mixture of the sulphates of potash, of ammonia, and of protoxide of iron (303). When fused with dry carbonate of potash the ferrocyanide furnishes a convenient source of cyanide of potassium (1339). Ferrocyanide of potassium is manufactured in large quantities for use in dyeing and calico-printing; it produces a beautiful bright blue colour, which, however, will not bear washing with alkaline solutions, or with soap. It is used also in the preparation of Prussian blue, as well as in the processes of electro-plating and electro-gilding. It is the source from which all the compounds of cyanogen are obtained. An aqueous solution of ferrocyanide of potassium produces characteristic precipitates with many of the metallic salts; it is, consequently, extensively employed as a qualitative test for indicating the presence of metallic bodies in solution. The precipitate generally consists of a ferrocyanide of the metal by which the precipitate is occasioned; usually the 2 equivalents of potassium in the ferrocyanide are displaced by 2 equivalents of some other metal, such as cobalt, nickel, copper, or lead, yielding precipitates Co_2Fcy; Ni_2Fcy; Cu_2Fcy; Pb_2Fcy. These precipitates are apt to retain portions of the ferrocyanide of potassium, from which it is difficult to free them even by long-continued washing. In a few cases 1 equivalent of ferrocyanide of potassium combines with the ferrocyanide of the other metal, with which it forms an insoluble precipitate, as happens when a salt of baryta is precipitated; the yellowish-white precipitate consisting of $(Ba_2Fcy + K_2Fcy, 6Aq)$ or of $(KBa, Fcy, 3Aq)$. The insoluble ferrocyanides cannot be precipitated in alkaline solutions; the liquid, in all cases, should be slightly but distinctly acid. Many of these precipitates are white, such as those of zinc, cadmium, nickel, manganese, tin, lead, bismuth, antimony, silver, chalk, plaster of Paris, and starch. It always retains a portion of ferrocyanide of potassium.

Prussian blue, as met with in commerce, occurs in cubical or irregular masses of a dark blue colour, which when pressed with a hard body acquire a coppery lustre resembling that of indigo. It is insoluble in water and in weak acids, and has neither taste nor smell. After it has been washed with dilute hydrochloric acid, it may, however, be rendered soluble by triturating it with one-sixth of its weight of crystallized oxalic acid. When this is diluted with forty or fifty parts of water it forms a blue solution, which is used as a writing ink. Prussian blue is also soluble in a cold solution of tartrate of ammonia. It is decomposed when treated with alkalies or alkaline carbonates, oxide of iron being liberated, and ferrocyanide of the metal remaining in solution. Oil of vitriol produces a white pasty mass when triturated with Prussian blue, but on the addition of water sulphuric acid is separated, and the blue pigment is reproduced. Prussian blue is decomposed when heated with concentrated sulphuric, nitric, or hydrochloric acid: it is also decomposed by the action of chlorine.

Prussian blue contains water, which cannot be expelled by heat without decomposing the compound. If heated in the open air it becomes kindled on the approach of an ignited body, and burns like tinder, leaving a residue of peroxide of iron.

(1351) When protosalts of iron are mixed with a solution of ferrocyanide of potassium a greenish white precipitate is formed, which appears to be the same as Everitt's white salt (408), and may be regarded as a compound of cyanide of iron and ferrocyanide of potassium; $2\,(K_2, FeCy_3) + 2\,FeCl = (K_2, FeCy_3 + 3\,FeCy) + 2\,KCl$. When this white substance is exposed to the air the cyanide of iron becomes oxidized and turns blue, and a compound is formed termed ***soluble*** or ***basic Prussian blue;*** it consists of one equivalent of sesquioxide of iron combined with one equivalent of Prussian blue: the ferrocyanide of potassium originally present in the white compound may then be washed away. The change which occurs is probably the following, neglecting the ferrocyanide of potassium of the precipitate, as it is not affected; $9\,FeCy + O_3 = (Fe_7Cy_9 + Fe_2O_3)$. Basic Prussian blue is soluble in pure water, but is precipitated on adding a saline solution: a strong acid removes the sesquioxide of iron from it, and converts it into ordinary Prussian blue.

(1352) FERRIDCYANIDES.—*Ferridcyanide of Potassium*, or *Red Prussiate of Potash* (K_3, Fe_2Cy_6).—When a current of chlorine gas is passed through a dilute solution of ferrocyanide of potassium, the cadmium a yellow, with nickel a yellowish green, with cobalt a dark reddish brown, with copper a yellowish green, with protosalts of iron a brilliant blue, with manganese a brown, with protosalts of tin a white, with silver an orange, and with subsalts of mercury a brownish red. These precipitates, with the exception of those with zinc and tin, are insoluble in dilute hydrochloric acid. The following table exhibits the composition of some of the ferridcyanides :—

Ferridcyanogen (hypothetical)	$C_{12}N_6Fe_2$	Fdcy
Hydroferridcyanic acid .	$H_3C_{12}N_6Fe_2$	H_3, Fdcy
Ferridcyanide of potassium	$K_3C_{12}N_6Fe_2$	K_3, Fdcy
Ferridcyanide of sodium .	$Na_3C_{12}N_6Fe_2$, 2 HO	Na_3. Fdcy, 2 Aq
Ferridcyanide of sodium and potassium .	$K_3Na_3C_{24}N_{12}Fe_4$, 12 HO	K_3Fdcy, Na_3Fdcy, 12 Aq
Ferridcyanide of potassium and barium .	$KBa_3C_{12}N_6Fe_2$, 6 HO	KBa_3, Fdcy, 6 Aq
Ferridcyanide of iron (Turnbull's blue) .	$C_{12}N_6Fe_5$, xHO	Fe_3, Fdcy, xAq

Ferridcyanide of potassium gives no precipitate in the solutions of the persalts of iron, but a splendid blue when mixed with those of the protosalts. It is a very delicate test for protoxide of iron when in solution. If protosulphate of iron be employed, the change which occurs is the following; $K_3Fdcy + 3\,(FeO, SO_3) = Fe_3, Fdcy + 3\,(KO, SO_3)$. The precipitate which is thus formed constitutes a highly valued and brilliant variety of Prussian blue, commercially known as *Turnbull's Blue*. Turnbull's blue may be distinguished from ordinary Prussian blue by the action of a solution of potash upon it, which decomposes it into ferrocyanide of potassium and *magnetic* oxide of iron, whilst the ordinary blue when similarly treated yields sesquioxide of iron.

Williamson finds that when Everitt's white salt (KFe, Fcy) is treated with chlorine or with nitric acid it is decomposed, and a blue salt is formed (KFe_2, Fe_2Cy_6) corresponding in composition to Turnbull's blue, but containing an equivalent of potassium in the place of one of the equivalents of iron. The formation of this substance is best effected by boiling the white precipitate with nitric acid, diluted with twenty parts of water; as the liquid approaches the boiling point a copious evolution of binoxide of nitrogen occurs: two equivalents of the white salt lose one equivalent of potassium, and the ferridcyanide of potassium and iron is formed. Care is required to prevent the action of the acid from proceeding too far, otherwise the compound acquires a green colour, owing to the formation of Pelouze's magnetic cyanide of iron.

allowed to cool, by which means a large quantity of nitrate of potash, mixed with a small proportion of oxamide will be separated. The strongly-coloured mother liquor must next be neutralized with carbonate of potash or carbonate of soda, by which a greenish brown precipitate is caused; and the liquid, after filtration, must be evaporated and allowed to crystallize. The soda salt crystallizes more readily than the nitro-prusside of potassium, which is somewhat deliquescent, although an anhydrous salt.

Nitro-prusside of Sodium (Na_2, $Fe_2Cy_5NO_2$, 4 Aq).—This salt crystallizes in fine prisms of a ruby-red colour, which require about 2½ parts of cold water for solution. Its solution is decomposed by exposure in the sun's rays, Prussian blue being deposited, whilst binoxide of nitrogen escapes. *Nitro-prusside of Barium* (Ba_2, $Fe_2Cy_5NO_2$, 6 Aq) crystallizes in fine octohedra of a dark red colour.

The nitro-prussides give a pale green precipitate with salts of copper, and a flesh-coloured precipitate with those of silver. With salts of zinc a salmon-coloured precipitate is produced; with salts of nickel, a dirty white; with salts of cobalt, a flesh-coloured precipitate; and with protosalts of iron, a salmon-coloured precipitate is formed. The persalts of iron, and the salts of lead, of mercury, and of tin, give no precipitates with the nitro-prussides. Chlorine is without effect upon solutions of the nitro-prussides, but they are decomposed when boiled with the alkalies, and the solution becomes orange-coloured. Sulphuretted hydrogen also decomposes them. The most delicate and characteristic test for the nitro-prussides is the production of a magnificent purple colour when mixed with solutions of the alkaline sulphides. This coloration is extremely intense, and may be employed to indicate very minute traces either of a soluble sulphide or of a nitro-prusside. The colour, however, speedily disappears. It appears to be due to the formation of a double salt of the nitro-prusside with the sulphide of the alkaline metal.

(1354) COBALTICYANIDES.—When cyanide of potassium is added to a salt of cobalt, it gives a reddish brown precipitate (CoCy), which is soluble in excess of cyanide of potassium. The double cyanide of cobalt and potassium (KCy, CoCy) thus obtained is decomposed on the addition of hydrochloric acid, and the cyanide of cobalt is reprecipitated; but if, previously to the addition of hydrochloric acid, it be exposed to the air, it absorbs oxygen, and cobalticyanide of potassium is produced:—

$$2\,(\mathrm{CoCy,\ KCy}) + 2\,\mathrm{KCy} + \mathrm{O} = \mathrm{K_3,\ Co_2Cy_6} + \mathrm{KO}.$$

After this change has occurred, the addition of hydrochloric acid preceding series: for example, the following formulæ represent a few of the platino-cyanides :—

Hydroplatino-cyanic acid	$H, PtCy_2$.
Platino-cyanide of potassium . . .	$K, PtCy_2$, 3 Aq.
Platino-cyanide of cuprammonium .	$(CuH_3, N), PtCy_2$, Aq.

Platino-cyanide of Potassium may be formed either by dissolving protochloride of platinum in a solution of cyanide of potassium; or by fusing ferrocyanide of potassium with spongy platinum; or by heating a concentrated solution of bichloride of platinum with an excess of cyanide of potassium. This beautiful salt forms long transparent rhombic prisms, which are yellow by transmitted, and blue by reflected light: it is very soluble in water, and more sparingly so in alcohol and ether. *Platino-cyanide of magnesium* is a beautiful salt which crystallizes in rosettes from its solution in a mixture of alcohol and ether; these crystals form square prisms, and exhibit various shades of crimson, of green, and of blue; they are very soluble in water, and the solution is nearly colourless. The most characteristic test of the platino-cyanides is the formation of a beautiful blue precipitate when a platino-cyanide is added to a solution of subnitrate of mercury in excess; but if the platino-cyanide be in excess the precipitate is white. A double salt of copper and ammonia $[(CuH_3, N) PtCy_2, Aq]$ is obtained by adding platino-cyanide of potassium to an ammoniacal solution of nitrate of copper: in the course of a few hours the salt is deposited in dark blue needles.

(1357) The *Platinic-cyanide* (*sesquiplatino-cyanide*) *of Potassium* (K_2, Pt_2Cy_5, 6 Aq) is another very beautiful salt which crystallizes in prisms of a coppery lustre when viewed by reflected light, but they appear green by transmitted light; its solution, however, is colourless. This salt is easily decomposed by a moderate heat; when dissolved in water it produces a white precipitate with salts of silver and of red oxide of mercury, a blue with the subsalts of mercury, and a greenish-blue with salts of copper. Sesquiplatino-cyanide of potassium is obtained by transmitting chlorine through a saturated solution of the platino-cyanide of potassium ($K, PtCy_2$) when the liquid becomes filled with crystalline needles of the new salt. It must be purified by pressure between folds of blotting-paper, and recrystallized from a very small quantity of boiling water acidulated with hydrochloric acid. An excess of potash reconverts it into the platino-cyanide. For further details respecting the platino-cyanides, see Knop, Liebig's *Annal.* xliii. 111; and Quadrat, *ib.* lxiii. 164, and lxx. 300.

not known in a separate condition, but it forms an acid compound with hydrogen, and yields numerous well-marked salts. Some chemists prefer to regard the sulphocyanides as representatives of the cyanates, in which the oxygen of the latter salts has had its place supplied by sulphur; and the decomposition of hydrosulphocyanic acid by the aid of heat and acids resembles that of cyanic acid under similar circumstances :—

$$\overbrace{2\,(\mathrm{H},\ \mathrm{C_2NS_2})}^{\text{Hydrosulphocy. Acid.}} + 4\,\mathrm{HO} = 2\,\mathrm{CO_2} + 2\,\mathrm{CS_2} + 2\,\mathrm{H_3N};$$

$$\overbrace{2\,(\mathrm{H},\ \mathrm{C_2NO_2})}^{\text{Cyanic Acid.}} + 4\,\mathrm{HO} = 2\,\mathrm{CO_2} + 2\,\mathrm{CO_2} + 2\,\mathrm{H_3N}.$$

Sulphocyanide of ammonium would then correspond to a sulphuretted urea, as cyanate of ammonia does to ordinary urea. The following table represents both views :—

Hydrosulphocyanic acid . .	HS, CyS	H, Scy
Sulphocyanide of potassium .	KS, CyS	K, Scy
Sulphocyanide of sodium .	NaS, CyS	Na, Scy
Sulphocyanide of ammonium	$\mathrm{H_4NS}$, CyS	$\mathrm{H_4N}$, Scy
Sulphocyanide of calcium .	CaS, CyS, 3 HO	Ca, Scy, 3Aq
Sulphocyanide of copper . .	CuS, CyS	Cu, Scy
Disulphocyanide of copper .	$\mathrm{Cu_2S}$, CyS	$\mathrm{Cu_2}$, Scy
Sulphocyanide of lead . .	PbS, CyS	Pb, Scy
Sulphocyanide of silver and of potassium	AgS, CyS+KS, CyS	Ag, Scy+K, Scy
Sulphocyanide of mercury and of potassium . . .	HgS, CyS+KS, CyS	Hg, Scy+K, Scy
Disulphocyanide of mercury	$\mathrm{Hg_2S}$, CyS	$\mathrm{Hg_2}$, Scy

The view which admits the existence of sulphocyanogen as the salt-radicle of these compounds is the one which is generally adopted, and since it renders a simple and satisfactory account of the metamorphoses to which the sulphocyanides are subject, it will be made use of here.

The sulphocyanides of *sodium* and of *ammonium* are anhydrous and deliquescent. Small quantities of one of these salts exists in the saliva of man and of the sheep. The majority of the sulphocyanides are soluble both in water and in alcohol; their most characteristic property is the production of an intense blood-red colour when their solutions are mixed with those of the persalts of iron: if the red liquid thus formed be acidulated with hydrochloric acid, and fragments of zinc be added, sulphuretted hydrogen is disengaged, and the colour disappears. The persulphocyanide of iron does not form crystals. Sulphocyanide of becomes semi-solid from the separation of *hydropersulphocyanic* acid (H_2, Cy_2S_6) in crystalline needles. These crystals are sparingly soluble even in boiling water, and as the solution cools it deposits the acid in beautiful orange-coloured needles.

(1361) *Mellon* ($C_{18}N_{13}$; Liebig).—This anomalous compound was originally supposed by Liebig to contain C_6N_4, but he has recently repeated and varied his experiments upon it, and has altered its formula as above. Mellon is not known in an isolated form in a state of purity, but it constitutes the principal portion of the solid residue obtained by heating the yellow precipitate occasioned by chlorine in solutions of the sulphocyanides. Mellon appears to be a tribasic radicle, which forms with hydrogen an acid termed *hydromellonic* acid ($H_3, C_{18}N_{13}$); this latter is an unstable compound which yields three salts with potassium; a neutral mellonide, $K_3, C_{18}N_{13}$, 10 Aq; a soluble acid mellonide, $K_2H, C_{18}N_{13}$, 6 Aq; and an insoluble acid mellonide, $KH_2, C_{18}N_{13}$. The neutral mellonide is usually formed as a secondary product during the preparation of sulphocyanide of potassium; but it is more plentifully obtained by fusing 3 parts of pure sulphocyanide of potassium, and gradually adding about one part of crude mellon; it is very soluble in hot water, from which it crystallizes on cooling with 10 Aq. Its solution has an intensely bitter taste. A solution of mellonide of potassium produces white insoluble mellonides when mixed with solutions of nitrate of silver, of corrosive sublimate, and of acetate of lead.

When mellonide of potassium is boiled with an excess of potash it is decomposed, and a new tribasic acid, the *cyameluric* ($3\,HO, C_{12}N_7O_3$) is formed: various other compounds are also obtained by its decomposition; for details regarding which the reader is referred to Liebig's paper (Liebig's *Annal.* xcv. 257).

(1362) *Melam.*—When sulphocyanide of ammonium is submitted to distillation it undergoes decomposition, and yields a mixture of bisulphide of carbon, sulphuretted hydrogen, and ammonia, whilst there remains in the retort a grey insoluble residue, which Liebig has called *melam* ($C_{12}H_9N_{11}$, Liebig; or $C_6H_6N_6$, Gerhardt; calculating from Voelckel's analysis):—

$$\overbrace{8\,(H_4N,\ C_2NS_2)}^{\text{Sulphocyan. Ammon.}} = 4\,CS_2 + 8\,HS + 5\,H_3N + \overbrace{C_{12}H_9N_{11}}^{\text{Melam.}}.$$

The same substance may be procured by heating an intimate may be seen by the following equations, which illustrate the relations of composition which they all bear to cyanuric acid :—

$$\begin{array}{lll}
\text{Melamine . .} & C_6H_6N_6 = & \overbrace{3\,HO, C_6N_3O_3}^{\text{Cyanuric Acid.}} + 3\,H_3N - 6\,HO \\
\text{Ammeline . .} & C_6H_5N_5O_2 = & 3\,HO, C_6N_3O_3 + 2\,H_3N - 4\,HO \\
\text{Melanuric acid} & C_6H_4N_4O_4 = & 3\,HO, C_6N_3O_3 + H_3N - 2\,HO \\
\text{Ammelid . .} & C_{12}H_9N_9O_6 = & 2(3\,HO, C_6N_3O_3) + 3\,H_3N - 6\,HO \\
\text{Cyameluric acid} & C_{12}H_3N_7O_6 = & 2(3\,HO, C_6N_3O_3) + H_3N - 6\,HO.
\end{array}$$

The formation of melamine and of ammeline from melam is readily explained, since

$$\overbrace{C_{12}H_9N_{11}}^{\text{Melam.}} + 2\,HO = \overbrace{C_6H_6N_6}^{\text{Melamine.}} + \overbrace{C_6H_5N_5O_2}^{\text{Ammeline.}}.$$

(1363) *Cyanuric Acid* (3 HO, $C_6N_3O_3$, 4 Aq).—This polymeride of cyanic acid may be obtained in various ways. 1. By the action of sulphuric acid upon melam or its derivatives, as just described. 2. By the action of a current of dry chlorine upon fused urea; sal-ammoniac, nitrogen, and hydrochloric acid, are thus produced, and cyanuric acid is formed in abundance: the sal-ammoniac may be removed by washing with cold water, and the cyanuric acid may be crystallized from boiling water. 3. By decomposing hydrochlorate of urea by heat: if the compound formed by transmitting dry hydrochloric acid gas over powdered urea be heated to 293° in an oil bath, rapid decomposition occurs, sal-ammoniac is sublimed, and pure cyanuric acid may be obtained by crystallizing the residue from boiling water; $3\,(C_2H_4N_2O_2, HCl) = 3\,(H_4NCl) + (3\,HO, C_6N_3O_3)$. 4. By heating urea beyond its fusing point until it has become converted into a dry greyish mass, resembling ammelid in appearance and properties: when this residue, which consists of melanuric acid ($C_6H_4N_4O_4$), is dissolved in hot oil of vitriol, to which a small quantity of nitric acid has been added for the purpose of removing the colour, cyanuric acid is deposited on diluting the liquid moderately with water. 5. By the destructive distillation of uric acid; cyanuric acid being one of the products obtained in this operation.

Cyanuric acid is deposited from its aqueous solution in colourless rhombic prisms, which are efflorescent. It is sparingly soluble in cold water, more freely so in boiling water, and is also somewhat soluble in boiling alcohol. When crystallized from hot hydrochloric or nitric acid, it is deposited in square-based anhydrous octohedra. By long boiling with the concentrated acids it is decomposed into carbonic acid and ammonia. When crystallized cyanuric acid is distilled, it is converted into hydrated cyanic acid, and this hydrate in a few minutes begins to undergo a spontaneous change into the white insoluble compound known as ***cyamelid*** (411), while the temperature rises spontaneously, owing to the solidification of the mass.

Cyanuric acid is generally considered to be tribasic;* its salts with lead and with silver contain 3 equivalents of a metallic oxide. Most of the cyanurates are sparingly soluble in water. Those of the alkalies and of the alkaline earths contain only two equivalents of fixed base. An acid cyanurate of ***ammonia*** (H_4NO, 2 HO, $C_6N_3O_3$ + 2 Aq) may be obtained in brilliant efflorescent prisms; and an acid cyanurate of ***potash*** (KO, 2 HO, $C_6N_3O_3$) is deposited in anhydrous cubes, when acetic acid is added in small quantities at a time to a solution of cyanate of potash, three equivalents of cyanic acid coalescing to form one equivalent of the polymeric cyanuric acid:—

$$\overbrace{3\,(KO, C_2NO)}^{\text{Cyanate of Potash.}}+2\overbrace{(HO, C_4H_2O_3)}^{\text{Acetic Acid.}}=2\overbrace{(KO, C_4H_3O_3)}^{\text{Acetate of Potash.}}+\overbrace{KO,\ 2\,HO, C_6N_3O_3}^{\text{Cyanurate of Potash.}}.$$

When a solution of a salt of copper, after being saturated with ammonia, is mixed with a solution of cyanuric acid, a characteristic violet precipitate, which is insoluble in cold water, is formed. Cyanurate of ***silver*** ($Ag_3O_3C_6N_3O_3$) is white, and insoluble in water, but soluble in dilute nitric acid. A cyanurate of silver, 2 AgO, HO, $C_6N_3O_3$, may also be obtained.

(1364) *Isomerides of Cyanuric acid.*—Sometimes during the preparation of cyanuric acid, by boiling crude mellon (1361) with nitric acid, crystals of an acid isomeric with the cyanuric are formed. It crystallizes in long oblique rhomboidal prisms which are efflorescent: it resembles cyanuric acid, but is distinguished from the latter by its greater solubility; Liebig terms it ***cyanilic acid.***

Fulminuric or *Isocyanuric acid,* (HO, $C_6N_3H_2O_5$).—This is an acid recently discovered about the same time by Liebig and by Schischkoff. Hydrated fulminuric acid contains the same elements as the hydrated cyanuric, but it is a monobasic acid, the elements of 2 equivalents of water being united with those of 3 of cyanogen and with oxygen to form the acid. The salts of fulminuric acid are obtained by boiling one of the fulminates, such as fulminate of mercury, with a solution of one of the soluble chlorides. When fulminate of mercury is thus boiled with chloride of potassium, it is gradually dissolved, and yellow oxide of mercury is separated: during the first part of the operation, the liquid appears turbid, but as soon as this appearance ceases it is filtered, and on being evaporated it yields brilliant crystals of fulminurate of potash. The decomposition may be thus represented:—

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* Wöhler regards cyanuric acid as dibasic, and considers that 1 equivalent of water enters into the composition of the acid. (Liebig's *Annal.* lxii. 241.)

$$\overbrace{3\,(Hg_2O_2,\ C_4N_2O_2)}^{\text{Fulminate of Mercury.}} + 4\,HO + 2\,KCl = \overbrace{2\,(KO,\ C_6N_3H_2O_5)}^{\text{Fulminurate of Potash.}}$$
$$+ 4\,HgO + 2\,HgCl.$$

In short, the elements of 3 equivalents of fulminic acid become condensed and form 2 equivalents of fulminuric acid. The fulminurates crystallize with great facility; they possess a high lustre and exert a great dispersive power on light; they are decomposed by heat with a feeble explosion.

It thus appears (supposing fulminic acid to be capable of existing in the form of a hydrate) that not less than 6 compounds polymeric with cyanuric acid might be produced, viz.:—

Cyanuric acid . . $C_6H_3N_3O_6 = 3\ HO,\ C_6N_3O_3$
Cyanilic acid . . $C_6H_3N_3O_6 = 3\ HO,\ C_6N_3O_3$
Fulminuric acid . $C_6H_3N_3O_6 = HO,\ C_6H_2N_3O_5$
Fulminic acid . . $C_4H_2N_2O_4 = 2\ HO,\ C_4N_2O_2$
Cyanic acid . . $C_2H\,N\,O_2 = HO,\ C_2N\,O$
Cyamelid . . . $C_2H\,N\,O_2 = HN,\ C_2O_2$

It is a remarkable peculiarity of cyanogen both when free and when in combination, that it exhibits a strong tendency to form new compounds by condensation; thus paracyanogen is formed by the condensation of several molecules of cyanogen into a single more complex molecule: in like manner the liquid and solid chlorides of cyanogen are produced by the condensation of several molecules of the gaseous chloride into one, and the molecule of cyanuric acid may be obtained by the condensation of 3 molecules of cyanic acid into one complex molecule.

(1365) The action of ammonia upon the oxygen acids of cyanogen has not been fully studied: the group of bodies derived from melam appears to be intimately related to the amides of cyanuric acid, and would well repay further investigation. The compounds of cyanic acid with ammonia are still more interesting, since they include the remarkable substance known as urea. This substance has the composition of cyanate of ammonia, and it is always produced when a solution of cyanate of ammonia is evaporated. True cyanate of ammonia may be obtained by transmitting the vapour of hydrated cyanic acid into gaseous ammonia, when it is

(1367) 1. UREA ($C_2H_4N_2O_2$).—This important compound is an essential constituent of the urine of animals; it is abundant in that of the mammalia, and particularly so in the urine of the carnivora; but it has also been met in the urine of birds, and of amphibia. Urea is the principal outlet for the nitrogen of the system, after the materials which compose the animal tissues have experienced oxidation under the influence of the respired air, a healthy human adult excreting about an ounce of urea daily. Dumas made many fruitless attempts to effect the direct conversion of the azotised constituents of the body into urea; but Béchamp has recently succeeded in obtaining this result by subjecting albumen to the oxidizing action of permanganate of potash.—(*Annales de Chimie*, III. xlviii. 348.) Urea is not formed in the kidneys; these glands appearing to act somewhat in the manner of filters, by means of which the urea is separated from the mass of the blood, in which it exists already formed before reaching the kidneys.

Urea may be obtained artificially in a variety of ways, one of the most remarkable of which was discovered by Wöhler, who showed that cyanate of ammonia, which is metameric with urea, when evaporated at a gentle heat, furnishes urea:—

$$\overbrace{H_4NO,\ C_2NO}^{\text{Cyanate of Ammonia.}} \quad = \quad \overbrace{C_2H_4N_2O_2}^{\text{Urea.}}.$$

This conversion of the cyanate into urea occurs whether it be formed by the direct union of hydrated cyanic acid with ammonia, or by the double decomposition of a metallic cyanate, such as cyanate of potash, with a salt of ammonia. Neither cyanic acid nor ammonia can, however, be discovered in the compound obtained; but if a solution containing a mixture of nitrate of silver and urea be boiled for some time, it is partly resolved into cyanate of silver and nitrate of ammonia.

Urea is likewise formed during the action of peroxide of lead and other oxidizing agents upon uric acid; by the action of alkalies upon alloxan, and upon kreatine; as well as by the action of sulphuretted hydrogen upon the fulminate of mercury or of silver. It is also obtained as a product of the action of oxychloride of carbon upon ammonia, and by the re-action of ammonia upon carbonic ether, at a temperature of 360°. (1006; Natanson.) Urea is isomeric with carbamide, if not identical with it; $C_2H_4N_2O_2 = \left.\begin{matrix}C_2O_2\\ H_2\\ H_2\end{matrix}\right\}N_2.$

soluble in water and in hot alcohol, but very sparingly so in ether. It forms no definite compound with water, but it deprives many salts, such as sulphate of soda, of their water of crystallization when triturated with them, producing a soft semi-fluid magma. Urea melts at about 248°, but at a temperature a little above this it is decomposed, yielding ammonia and carbonate of ammonia, whilst a white amorphous residue, consisting of melanuric acid, is obtained:—

$$4\,\overbrace{(C_2H_4N_2O_2)}^{\text{Urea.}} = \overbrace{C_6H_4N_4O_4}^{\text{Melanuric Acid.}} + 2\,CO_2 + 4\,H_3N.$$

Previous to the completion of this change, a substance termed *biuret* ($C_4H_5N_3O_4$, 2 Aq) is formed (1372).

A solution of urea, if pure, may be kept at ordinary temperatures without alteration, and it may even be boiled without undergoing decomposition; but if heated in a sealed tube to about 284° it combines with 4 equivalents of water, and is converted into carbonate of ammonia:—

$$\overbrace{C_2H_4N_2O_2}^{\text{Urea.}} + 4\,HO = \overbrace{2\,(H_4NO,\,CO_2)}^{\text{Carb. Ammonia.}}.$$

The same change takes place slowly at ordinary temperatures in the presence of the mucus of the bladder, the ammoniacal odour acquired by urine after keeping it for a few days being due to this alteration. A similar decomposition into carbonic acid and ammonia occurs when urea is fused with hydrate of potash, or treated with concentrated sulphuric acid.

Chlorine, when transmitted into an aqueous solution of urea, resolves the latter into carbonic acid and nitrogen, whilst hydrochloric acid is formed:—

$$C_2H_4N_2O_2 + 2\,HO + 6\,Cl = 2\,CO_2 + 2\,N + 6\,HCl.$$

Urea does not possess well-marked basic properties, but it combines with certain acids, and yields crystallizable compounds, which preserve a strong acid reaction. It absorbs hydrochloric acid gas, forming a deliquescent mass ($C_2H_4N_2O_2$, HCl) which fuses at a gentle heat to a yellowish oil, and solidifies to a crystalline radiated mass as it cools; water decomposes it immediately. The most important salts of urea are those which it forms with nitric and oxalic acids. In combining with the oxyacids, urea unites with 1 equivalent of acid and 1 of water. *Nitrate of urea* ($C_2H_4N_2O_2$, HO, NO_5) is a compound which crystallizes in rhombic prisms, or in brilliant leaflets which are sparingly soluble in water, especially if it contain excess of nitric acid. It is sparingly soluble in alcohol. *Oxalate of urea* [2 ($C_2H_4N_2O_2$), 2 HO, C_4O_6 lizes in long thin transparent sparingly soluble pris almost insoluble in a saturated aqueous solution of oxal

(1368) *Compounds of Urea with Salts, and with Metalli* —Urea forms definite compounds with certain metalli such as those of silver and of mercury. Its compound wi ($3\,AgO, C_2H_4N_2O_2$) is produced by digesting at a gentle hea precipitated oxide of silver in an excess of a solution of a grey or yellowish crystalline powder is thus formed. such compounds may be obtained with red oxide of mer $C_2H_4N_2O_2$, 2 HgO; $C_2H_4N_2O_2$, 3 HgO; and $C_2H_4N_2O_2$, 4 The first of these compounds ($C_2H_4N_2O_2$, 2 HgO) is for successive portions of red oxide of mercury suspended in wa mixed with a warm solution of urea; at first the oxide of m is completely dissolved, but the compound in question is gra deposited as a white powder, which becomes yellowish on d The compound ($C_2H_4N_2O_2$, 3 HgO) is obtained by adding solution of urea rendered alkaline by potash, a solution of cor sublimate, taking care to maintain an excess of alka white gelatinous precipitate is formed, which when well wa is converted by boiling water into a pale yellow granular po having the composition above indicated; and the comp ($C_2H_4N_2O_2$, 4 HgO) is obtained by precipitating a soluti nitrate of the red oxide of mercury by adding it to an alk solution of urea. (Liebig, *Chem. Gaz.*, xii. 41.)

When a solution of the nitrate of red oxide of mercury (mer nitrate) is mixed with one of urea, the urea enters into combi tion with the salt in several proportions. If warm dilute solu of urea and the mercurial nitrate be mixed, a crystalline precip ($4\,HgO, NO_5, C_2H_4N_2O_2$) falls as a heavy granular powder, wh consists of concentric groups of minute needles. But if a di solution of the nitrate of mercury be added to a solution of u so long as a precipitate is formed, and the whole be maint at a temperature of from 104° to 122° F., the precipitat principally composed of six-sided prisms, consisting of (3 H $NO_5, C_2H_4N_2O_2$). If a solution of nitrate of urea be poured a somewhat dilute solution of nitrate of mercury, slightly ac lated with nitric acid, until a permanent turbidity appears filtering the liquid and allowing it to stand, crystalline crus small shining rectangular tables are gradually formed (2 H $NO_5, C_2H_4N_2O_2$).

Nitrate of silver forms two similar compounds, (AgO, $C_2H_4N_2O_2$) and [2 (AgO, NO [illegible] $_2O_2$], which cryst readily when a mixture of a solution of urea and of nitrate of silver is evaporated *in vacuo* over sulphuric acid. Urea also combines with other salts, but the compounds which it forms with them are of little importance.

(1369) *Liebig's method of determining Chlorides and Urea in Urine.*—The foregoing observations are due to Liebig, who has founded upon them a method of determining the quantity of chlorine and of urea in urine, which is valuable when such analyses are numerous, since it enables a large number of comparative experiments to be made in a short time.

1. *For the Chlorine.*—A solution of urea is not precipitated by a solution of corrosive sublimate, but it is immediately precipitated by the nitrate of the red oxide of mercury. Solutions of the chlorides of the metals belonging to the first two groups (439), when mixed with nitrate of mercury, become decomposed into corrosive sublimate, and a nitrate of the alkaline or earthy base; hence, when a solution of chloride of sodium is mixed with one of urea, no precipitate is occasioned in this liquid on the addition of nitrate of mercury, until the whole of the chloride of sodium has been decomposed by the mercurial salt; $NaCl + HgO, NO_5$ becoming $NaO, NO_5 + HgCl$. After this point has been reached, every fresh addition of the mercurial nitrate occasions a precipitate of the compound ($4\,HgO, NO_5, C_2H_4N_2O_2$); and if a solution of the mercurial salt of known strength and free from excess of acid be prepared, it is easy to determine the quantity of chlorides present by measuring the volume of this solution which it is necessary to add to a given volume of urine before it begins to occasion a precipitate.

2. *For the Urea.*—Having ascertained the number of divisions of the mercurial solution which are consumed before a precipitate begins to be formed, a measured volume of a standard solution of nitrate of silver, sufficient exactly to effect precipitation of the chlorine thus indicated, is added, and afterwards the urea is determined by means of the solution of nitrate of mercury. The following are the details of the operation:—

1. *Preparation of the Solution of Nitrate of Mercury No. 1, employed for determining the Chlorine.*—Pure crystals of subnitrate of mercury are to be dissolved in moderately strong nitric acid, and the solution is to be heated until a sample is no longer rendered turbid by chloride of sodium. The solution is next to be evaporated on a water-bath to a syrupy consistence, and diluted with about ten times its bulk of water; it is then set aside for twenty-four hours, and, if necessary, filtered. In order to graduate the solution, it

is necessary to procure a saturated solution o
sodium, prepared by digesting a large excess o
water, with frequent agitation, for twenty-four
grain measures of such a solution contain 31·84 gr
sodium. 150 grain measures of this solution (=
chloride of sodium) are poured into a small beaker,
45 grains of a solution of urea, containing about 4 p
and also with 75 grains of a cold saturated solution o
of soda; the solution of nitrate of mercury is then to b
mixture from a burette, with constant stirring, until a
pitate is permanently formed. The number of divisio
tion poured from the burette indicates the amount
which corresponds to 47·76 grains of chloride of so
strength of the mercurial solution having been thus asce
a proportion of water must be added to it, that 100
measures may correspond to 1 grain of chloride of sodi

2. *Preparation of the Solution of Nitrate of Silver*
for removing the Chlorine.—174·36 grains of fused
silver are dissolved in water, and diluted until the liquid
to 6000 grain measures; 100 grain measures of this solu
respond to 1 grain of chloride of sodium.

3. *Preparation of the Solution of Nitrate of Mercury N*
determining the Urea.—A concentrated solution of nitrate
cury, containing about 25 grains of the salt in 180 grain me
is prepared according to the directions already given. In
to graduate this solution, 60 grains of pure urea are to be disso
water, and diluted till the volume of the solution amounts to ex
3000 grains: 150 grain measures of this liquid are to be poured
a beaker, and the mercurial solution is to be added from a bur
till a few drops in a watch-glass produce a distinct yellow col
with carbonate of soda. If the solution were of the exact streng
desired, it would require 300 grain measures of the mercurial so
tion; but if the latter be prepared of the strength above directed
somewhat smaller quantity will be required, and a quantity of wa
exactly sufficient to reduce it to this strength must be added to the
solution.

It will be found convenient, in executing analyses of urine b
this method, to be provided, 1. with a pipette capable of delivering
exactly 225 water grains from a mark upon its stem, for meas
ing off the diluted urine; 2. with a small burette divided into grai
measures of water, and capable of measuring 100 grains, for the
mercurial solution No. 1; and 3. with an ordinary alkalimetr
burette (Fig. 290, Part II.), for the mercurial solution No. 2.

Before determining the urea in urine, it is necessary to remove the phosphoric acid contained in the liquid. This is effected by means of a mixture of two volumes of cold saturated baryta water, and one volume of a cold saturated solution of nitrate of baryta. A glass cylinder of about one ounce in capacity is filled to overflowing with urine, the excess being removed by causing a glass plate to slide over the mouth of the cylinder; two such cylinderfuls are to be poured into a beaker, and mixed with one cylinderful of the baryta solution. The precipitate thus formed is to be filtered off, and the amount of chloride of sodium in 225 grain measures of the filtrate (= 150 grains of urine) is to be determined by adding the standard solution of mercury No. 1, till a cloudiness appears: 450 grains more of the filtrate (=300 grains of urine) are then to be measured off into a separate vessel, and mixed with a quantity of the standard solution of silver, equal to twice that of the mercurial solution employed in the preceding experiment. The liquid is to be filtered, and a bulk of the filtrate, equal to 225 measured grains + half the volume of silver solution used, is to be employed for the determination of the urea. This quantity, which corresponds to 150 grains of urine, is to be poured into a beaker, and the graduated mercurial solution No. 2 added from a burette, with frequent stirring, until no further increase of the precipitate is perceptible. In order to ascertain whether a sufficient quantity of the mercurial solution has been added, a few drops of the turbid liquid are to be removed with a pipette into a watch-glass, and 2 or 3 drops of a solution of carbonate of soda allowed to flow from the edge of the glass into the liquid. If, after some minutes, the mixture retain its white colour, a further quantity of the mercurial solution is to be added, until a fresh sample plainly exhibits the yellow colour after the addition of the carbonate of soda.

Picard has successfully applied a modification of this method to the detection of urea in healthy blood, and he has even succeeded in estimating the difference in the quantity of urea contained in the blood of the renal artery, and in that of the renal vein after the blood has undergone the depurating influence of the kidney. (*Comptes Rendus*, Sept. 8, 1856.)

(1370) *Compound Ureas.*—A remarkable series of compounds may be obtained from urea by the displacement of a certain number of the equivalents of hydrogen which it contains. The formation of these compounds is most readily explained upon the hypothesis that urea is the diamide (1051) of carbonic acid, this acid being regarded, as Gerhardt considers it, in the light of a dibasic acid:

(C_2O_2) would then occupy the place of H_2 in the d of ammonia; thus urea $C_2H_4N_2O_2 = \left.\begin{matrix}C_2O_2\\H_2\\H_2\end{matrix}\right\}N_2$, a four equivalents of hydrogen would admit of displa organic radicle. Compounds of this kind are readily fo cases by the action of cyanic acid upon the base which sent, just as ordinary urea is formed from ammonia, upon it with cyanic acid. They may also be obtained posing the cyanic ethers with ammonia. The compo combine, like ordinary urea, with acids, and form cry salts. Examples of the formation of these compounds ha occurred in the case of the alcohol radicles (1007); thus we

Ethyl-urea $= C_6H_8N_2O_2 = \left.\begin{matrix}C_2O_2\\C_4H_5\\H_3\end{matrix}\right\}N_2$, or $\begin{matrix}C_4H\\HO,\end{matrix}$

Ethyl-methyl-urea $= C_8H_{10}N_2O_2 = \left.\begin{matrix}C_2O_2\\C_4H_5\\C_2H_3\\H_2\end{matrix}\right\}N_2$, or $\begin{matrix}C_6H_9N\\HO,C\end{matrix}$

Tetrethyl-urea . $= C_{18}H_{20}N_2O_2 = \left.\begin{matrix}C_2O_2\\2(C_4H_5)\\2(C_4H_5)\end{matrix}\right\}N_2$, or $\begin{matrix}C_{16}H_{20}N\\CyO\end{matrix}$

Phenyl-urea (carbanilamide) $\Big\} = C_{14}H_8N_2O_2 = \left.\begin{matrix}C_2O_2\\C_{12}H_5\\H_3\end{matrix}\right\}N_2$, or $\begin{matrix}C_{12}H_7N,\\HO,CyO\end{matrix}$

Diphenyl-urea (flavine) $\Big\} = C_{26}H_{12}N_2O_2 = \left.\begin{matrix}C_2O_2\\2(C_{12}H_5)\\H_2\end{matrix}\right\}N_2$,

Phenyl-ethyl-urea $= C_{18}H_{12}N_2O_2 = \left.\begin{matrix}C_2O_2\\C_{12}H_5\\C_4H_5\\H_2\end{matrix}\right\}N_2$.

It is obvious that this class of compounds admits of bein multiplied and varied as extensively as the allied group of arti cial bases. Some of the natural organic bases, such as nicoti and conia, when made to act upon the cyanic ethers, also react like ammonia, and give rise to bodies belonging to the class of ureas.

(1371) *Ureides.*—Urea likewise gives rise to the formation of a class of compounds analogous to the amides, forming substances which have been called *ureides*; that is to say, salts of urea from which the elements of water have been abstracted. When, for instance, a mixture of two equivalents of urea with one equivalent of one of the oxychlorides of the acids (1097) is heated, decomposition occurs, and a ureide is formed. Thus, if urea be heated to 300°, or 310°, and then gradually mixed with chloride of benzoyl, taking care that the temperature shall not exceed 320°, the mass becomes pasty, the odour of chloride of benzoyl disappears, and *benzureide* is left in the form of a crystalline powder, which is soluble in alcohol but insoluble in ether:—

$$\overbrace{C_{14}H_5O_2Cl}^{\text{Chlor. Benzoyl.}} + \overbrace{H_4N_2C_2O_2}^{\text{Urea.}} = \overbrace{H_3,\ C_{14}H_5O_2,\ N_2C_2O_2}^{\text{Benzureide.}} + HCl.$$

Chloride of othyl, chloride of butyryl, and chloride of valeryl, may be made in like manner to yield respectively *acetureide* (H_3, $C_4H_3O_2$, $N_2C_2O_2$); *butyrureide* (H_3, $C_8H_7O_2$, $N_2C_2O_2$); and *valerureide* (H_3, $C_{10}H_9O_2$, $N_2C_2O_2$). (Zinin.)

Besides these ureides, there are various compounds known which bear a relation to urea similar to that of the amidated acids to ammonia:—for example, allophanic acid (1008; HO, $C_4H_3N_2O_5$) may be regarded as *carbureic acid*, analogous to carbamic acid: oxaluric acid (1388) may in like manner be viewed as oxalureic acid; whilst parabanic acid (1389) would represent the imide corresponding to oxaluric acid (Gerhardt) thus:—

$$\overbrace{HO,\ H_2NC_2O_3}^{\text{Carbamic Acid.}} = \overbrace{H_3N,\ 2\ HO,\ C_2O_4}^{\text{Bicarbonate of Ammonia.}} - 2\ HO;$$

$$\overbrace{HO,\ C_2H_3N_2O_2,\ C_2O_3}^{\text{Allophanic Acid.}} = \overbrace{C_2H_4N_2O_2,\ 2\ HO,\ C_2O_4}^{\text{Hypothetical Carbonate of Urea and Water.}} - 2\ HO;$$

$$\overbrace{HO,\ C_2H_3N_2O_2,\ C_4O_5}^{\text{Oxaluric Acid.}} = \overbrace{C_2H_4N_2O_2,\ 2\ HO,\ C_4O_6}^{\text{Hypothetical Oxalate of Urea and Water.}} - 2\ HO;$$

$$\overbrace{2\ HO,\ C_6N_2O_4}^{\text{Parabanic Acid.}} = \overbrace{C_2H_4N_2O_2,\ 2\ HO,\ C_4O_6} - 4\ HO.$$

(1372) *Biuret* ($C_4H_5N_3O_4$, 2 Aq = HO, H_4NO, 2CyO, 2 Aq).—This compound has the composition due to bicyanate of ammonia, to which it appears to stand in a relation similar to that which exists between urea and cyanate of ammonia. It is prepared by melting urea for some time in an oil bath at a temperature between 300° and 340°. When the disengagement of ammonia has ceased and the mass kreatinine remains unchanged. Both kreatine and kreatinine were originally discovered among the constituents of the fluids contained in muscular tissues, whence they derive their name, from κρέας, flesh. There can be little doubt but that they are products of disintegration of the muscular tissue, and that, like urea, they are destined either for ulterior change in the economy, or for immediate rejection as excrementitious matter.

2. *Kreatine* ($C_8H_9N_3O_4, 2Aq$).—Kreatine is present in the juice of the flesh in very small proportion, a pound of flesh yielding on an average, according to Gregory, about five grains; the quantity, however, varies in the flesh of different animals. The flesh of the common fowl was found by Gregory to contain more kreatine than that of any animal upon which his experiments were made; but cod fish is the cheapest source of kreatine: 10,000 parts of fresh cod furnish from 9 to 17 parts of kreatine, whilst the same weight of fowl furnishes 32 parts. The best process consists in chopping up raw cod finely, mixing it with an equal weight of water, and expressing the liquid. This liquid is next heated sufficiently to coagulate the albumen, taking care to avoid ebullition, after which it is filtered. Baryta water is then added cautiously, so long as it occasions a precipitate; the liquid is again filtered, to separate the phosphate of baryta; and the filtrate, on being evaporated to a very small bulk, yields crystals of nearly pure kreatine. It may be rendered quite pure by a second crystallization.

Kreatine crystallizes in colourless, transparent, brilliant, oblique prisms, which, when heated to 212°, become opaque, and lose their water of crystallization. Kreatine is sparingly soluble in cold water, of which it requires 75 times its weight for solution; it is freely dissolved by boiling water. Alcohol, when cold, scarcely dissolves it; it is insoluble in ether. The aqueous solution has a weak, bitterish taste. Although kreatine is neutral to test papers, it forms definite compounds with some of the acids. The *hydrochlorate of kreatine* ($C_8H_9N_3O_4$, HCl) forms colourless, well-defined crystals, which are soluble in water. It may be prepared by mixing solutions of equivalent quantities of hydrochloric acid and kreatine, and evaporating in *vacuo*, or by a temperature not exceeding 90°. The *sulphate* ($C_8H_9N_3O_4$, HO, SO_3) may be obtained in a similar manner; the *nitrate* ($C_8H_9N_3O_4$, HO, NO_5) may also be obtained in brilliant crystals, which have a very sour taste.

When kreatine is boiled with oxide of mercury the oxide is reduced, and a basic substance is formed, which Dessaignes calls

methyluramine ($C_4H_7N_3$). The same substance
by boiling kreatine with sulphuric acid and p
When a solution of binoxide of nitrogen is trans
a solution of nitrate of kreatine an abundant di
gas occurs; on neutralizing with potash, separating
crystallization, and adding nitrate of silver, a cry
pound is obtained (C_8H_5N, AgO, NO_5), composed
silver with a new base, to which Dessaignes assigns
C_8H_5N.

If kreatine be boiled with either sulphuric, h
nitric, or phosphoric acid, it is decomposed, losing 2
of water; whilst kreatinine is formed, and enters into co
with the acid:—

$$\overbrace{C_8H_9N_3O_4}^{\text{Kreatine.}} = \overbrace{C_8H_7N_3O_2}^{\text{Kreatinine.}} + 2\,HO.$$

Alkaline bodies produce with kreatine a different res
for instance, to a boiling solution of kreatine crystallized
of baryta, equal in weight to ten times that of the kr
be added, the kreatine is gradually decomposed, another new
termed *sarkosine* is formed, and urea is found in the liquid
equivalent of hydrated kreatine furnishing the elements of
equivalent of sarkosine and one of urea:—

$$\overbrace{C_8H_9N_3O_4}^{\text{Kreatine.}} + 2\,HO = \overbrace{C_2H_4N_2O_2}^{\text{Urea.}} + \overbrace{C_6H_7NO_4}^{\text{Sarkosine.}}$$

By continued boiling with baryta the urea itself is de
posed into ammonia, which is expelled during the ebullition, a
carbonic acid, which combines with the baryta.

(1374) 3. *Kreatinine* ($C_8H_7N_3O_2$).—This base may be p
cured from urine by the method already described (1373
may also be obtained by boiling kreatine with hydrochloric ac
hydrochlorate of kreatinine is thus formed, and from this the
may be separated by boiling it with hydrated oxide of lead
[illegible], a yellow, insoluble oxychloride of lead is formed, and th
[illegible] remains in solution. Its crystals require about twe
[illegible] water for solution, and they are still more soluble
[illegible] kreatinine is also dissolved abundantly by boiling alcohol
[illegible] on cooling. Its aqueous solution restores the blue
[illegible] litmus, and expels ammonia when heated with
[illegible] ammoniacal salts. It has a strong tendency to form
[illegible]: for example, if a solution of nitrate of silver
[illegible], be mixed with one of kreatinine, it

becomes converted into a magma of white needles, which are very soluble in boiling water; and a similar compound is formed when a solution of corrosive sublimate is substituted for that of nitrate of silver. The chloride of zinc and kreatinine ($C_8H_7N_3O_2$, ZnCl) is also sparingly soluble. With the salts of copper, kreatinine forms a blue crystallizable compound. Both the sulphate and the hydrochlorate of kreatinine may readily be obtained in crystals.

(1375) 4. *Sarkosine,* from σὰρξ, flesh ($C_6H_7NO_4$).—In order to prepare this alkali, the solution of kreatine must be boiled with ten times its weight of hydrated baryta until all odour of ammonia shall have disappeared. The excess of baryta is to be removed by a current of carbonic acid gas; the solution is to be boiled, filtered, and evaporated to the consistence of syrup, from which the sarkosine may be obtained in foliated crystals. In order to ensure its purity it may be converted into the form of sulphate, the aqueous solution of which may be decomposed by pure carbonate of baryta. Sarkosine crystallizes in right rhombic, perfectly transparent, colourless prisms, which are freely soluble in water, sparingly so in alcohol, and insoluble in ether. At a temperature a little above 212° they melt, and may be sublimed unchanged. Its aqueous solution has a sharp, sweetish, somewhat metallic taste, but has no action on vegetable colours. It forms crystallizable salts, which have an acid reaction. The sulphate ($C_6H_7NO_4$, HO, SO_3, Aq) crystallizes in colourless quadrangular cubes. With bichloride of platinum, sarkosine gives a double salt, which by spontaneous evaporation may be obtained in large yellow flattened octohedra ($C_6H_7NO_4$, HCl, $PtCl_2$, 2 Aq). Sarkosine is isomeric with alanine and carbamic ether (urethane), as well as with lactamide, but quite distinct from all these bodies in properties, and is distinguished from them by its insolubility in ether and in alcohol.

(1376) 5. *Methyluramine* ($C_4H_7N_3$).—When an aqueous solution of kreatine or of kreatinine is boiled with oxide of mercury, carbonic acid is evolved, the oxide is reduced, and on evaporating the solution a copious crystallization of oxalate of methyluramine takes place:—

$$\overbrace{2(C_8H_9N_3O_4)}^{\text{Kreatine.}}+10\,HgO=\overbrace{2\,C_4H_7N_3,\ 2\,HO,\ C_4O_6}^{\text{Oxalate of Methyluramine.}}+4\,CO_2+2\,HO+10\,Hg.$$

When the oxalate of the base is decomposed by milk of lime, methyluramine is liberated, and may be obtained in the form of a colourless deliquescent mass, by evaporating the solution *in vacuo.* It is powerfully alkaline, and absorbs carbonic acid rapidly from the air. It has a caustic, somewhat ammoniacal taste. When heated on nine. Indeed, the true amides are all decomposed into salts of ammonia when boiled with dilute acids, whereas the compounds of the glycocine series may be boiled with dilute acids for hours without decomposition.

(1378) 6. *Glycocine* or *Glycocoll* ($C_4H_5NO_4$ or $C_4H_4NO_3$, HO).—This substance is one of the products of the decomposition of gelatin when boiled with dilute sulphuric acid; after removing the acid by means of carbonate of baryta, the glycocine may be procured in crystals on evaporating the solution. It may also be obtained by heating gelatin with solutions of potash or of soda. But it is most easily obtained in a state of purity by boiling hippuric acid with hydrochloric acid (1215); as the liquid cools, benzoic acid is separated in abundance, and glycocine remains in combination with hydrochloric acid:—

$$\overbrace{HO,\ C_{18}H_8NO_5}^{\text{Hippuric Acid.}} + HCl + 2\ HO = \overbrace{C_4H_5NO_4,\ HCl}^{\text{Hydrochlor. Glycocine.}} + \overbrace{HO,\ C_{14}H_5O_3}^{\text{Benzoic Acid.}}.$$

On the addition of absolute alcohol, after the solution has been concentrated by evaporation and supersaturated with ammonia, pure glycocine is deposited in minute crystals. Glycocine may also be obtained from glycocholic acid, one of the resinous acids of the bile (1439) when it is decomposed by ebullition with hydrochloric acid.

Pure glycocine has a sweet taste, which is less intense than that of cane-sugar: it is freely soluble in water, but less so in rectified alcohol; it is insoluble in absolute alcohol and in ether. Glycocine crystallizes readily by spontaneous evaporation of its aqueous solution. It is not susceptible of the alcoholic fermentation. Its solution has the power of reddening litmus feebly. It throws down metallic mercury from a solution of the sub-nitrate of this metal. Glycocine has a strong tendency to combine with the acids, without, however, neutralizing them; many of these compounds, such as the nitrate ($C_4H_5NO_4$, HO, NO_5), crystallize readily; the sulphate, the oxalate, and the hydrochlorate may also be obtained in crystals. A large number of the metallic oxides also combine with glycocine, displacing an equivalent of water from it, and forming with it soluble compounds, which may be obtained in crystals; this is the case with the oxides of zinc, of copper, of lead, of barium, and of silver. These compounds may be obtained by heating the hydrated oxides of the metals with a solution of glycocine. When glycocine is boiled with acetate of copper, acetic acid is expelled, and a compound of glycocine with oxide of copper is obtained in solution. If glycocine be heated with a strong solution of potash it gives a fleeting, beautiful fiery-by evaporation, and a considerable proportion of hydrochlorate of ammonia is separated in crystals. The mother liquors retain hydrochlorate of alanine. They must be boiled with hydrated oxide of lead, which is to be added in small portions to the boiling liquid until it ceases to occasion a disengagement of ammonia. The liquid is then to be decanted from the precipitate, heated with sulphuretted hydrogen to remove the excess of lead, filtered and evaporated. Alanine crystallizes out, and if the mother liquor be mixed with alcohol it furnishes an additional quantity. The reaction by which alanine is formed may be thus represented :—

$$\overbrace{H_3N, C_4H_4O_2}^{\text{Aldehyd Ammonia.}} + H, C_2N + HCl + 2\ HO = \overbrace{C_6H_7NO_4}^{\text{Alanine.}} + \overbrace{H_4N, Cl.}^{\text{Sal-ammoniac.}}$$

Alanine crystallizes in groups of colourless prisms, which are soluble in between four and five parts of cold water, but are very sparingly soluble in alcohol, and insoluble in ether. Its aqueous solution has a very sweet taste : it is without action upon test-papers. Alanine may be partially sublimed at a temperature a little above 400°. If heated suddenly, it melts and is decomposed ; when heated on platinum foil it burns with a violet flame. Hydrate of potash decomposes it, with disengagement of ammonia and of hydrogen, whilst acetate of potash and cyanide of potassium are obtained. When distilled with dilute sulphuric acid and peroxide of lead, carbonic acid, aldehyd, and ammonia are formed. But its most interesting metamorphosis is that which it undergoes when the aqueous solution is treated with nitrous acid, in which case lactic acid is formed, whilst nitrogen is liberated :—

$$\overbrace{2(C_6H_7NO_4)}^{\text{Alanine.}} + 2\ NO_3 = \overbrace{2\ HO, C_{12}H_{10}O_{10}}^{\text{Lactic Acid.}} + 2\ HO + 4\ N.$$

Alanine, like glycocine, forms numerous compounds both with acids and with bases ; many of them may be obtained in crystals, but they are all very soluble.

The compounds ($C_8H_9NO_4$) and ($C_{10}H_{11}NO_4$), intermediate between alanine and leucine, in the glycocine series, and corresponding to the aldehyd-ammonias of propionic and butyric acids, have not as yet been prepared.

(1380) 8. *Leucine, Caseous oxide* or *Aposepedine* ($C_{12}H_{13}NO_4$).—Various decompositions give rise to the formation of this body ; for example, it is one of the products of the putrefaction of casein, or of cheese, of muscle, and of gluten, in the presence of water ; it is also amongst the compounds obtained by the action either of sulphuric is sparingly soluble in cold water, but freely so in boiling water. The presence of acetic acid or of acetate of potash favours its solution both in water and in alcohol. Cold absolute alcohol dissolves it very sparingly, and it is insoluble in ether. It is however easily soluble in dilute solutions of the acids, with many of which it forms crystallizable compounds; the *hydrochlorate* of leucine ($C_{12}H_{13}NO_4$, HCl) is very soluble in water; the *nitrate* of leucine or nitroleucic acid ($C_{12}H_{13}NO_4$, HO, NO_5) crystallizes in colourless needles. An aqueous solution of leucine occasions a white precipitate with subacetate of lead; and if to a boiling solution of leucine mixed with the neutral acetate of lead ammonia be cautiously added, pearly scales (PbO, $C_{12}H_{13}NO_4$) are deposited. Leucine also precipitates subnitrate of mercury (Braconnot) but no other metallic solutions.

Leucine, when distilled with peroxide of lead furnishes ammonia and butyric aldehyd. If it be distilled with dilute sulphuric acid and peroxide of manganese, valeronitrile with carbonic acid and water are produced:—

$$\overbrace{C_{12}H_{13}NO_4}^{\text{Leucine.}} + 4\,O = \overbrace{C_{10}H_9N}^{\text{Valeronitrile.}} + 2\,CO_2 + 4\,HO.$$

If leucine be fused with hydrate of potash it yields valerate of potash, whilst ammonia and hydrogen are liberated:—

$$\overbrace{C_{12}H_{13}NO_4}^{\text{Leucine.}}+3\,(KO, HO)=\overbrace{KO,\, C_{10}H_9O_3}^{\text{Valerate of Potash.}}+2\,(KO,\, CO_2)+H_3N+4\,H.$$

Pure leucine is stated also to undergo a similar decomposition when caused to ferment, by the addition of a small quantity of muscular fibre, or of albumen. When an aqueous solution of leucine is submitted to the action of nitrous acid, the leucine is decomposed with liberation of nitrogen and the formation of *leucic acid* (2 HO, $C_{24}H_{22}O_{10}$), just as glycollic and lactic acids are formed from glycocine and alanine under similar circumstances.

(1381) 9. *Tyrosine* ($C_{18}H_{11}NO_6$; Hinterberger).—This substance was obtained by Liebig from the products of the fusion of well-dried cheese, fibrin, or albumen, with hydrate of potash, in the manner described when treating of the preparation of leucine. The crude crystals of tyrosine must be redissolved in a solution of potash, and precipitated with acetic acid. If coloured it must be converted into hydrochlorate, digested with animal charcoal, and the filtered liquid whilst boiling must be mixed with acetate of potash; chloride of potassium is thus formed, and tyrosine, free from acetic acid, is deposited in long fibrous crystals. Tyrosine is found among the products of the putrefaction of albumen, fib and casein, and it is produced together with leucine when the albuminoid bodies are boiled for some hours with dilute sulphu or hydrochloric acid. Horn, feathers, and hair, also yield it this treatment :—one part of horn, 4 of oil of vitriol, and water, if boiled for forty hours, furnish a dark brown fluid, wh at the end of that time must be rendered alkaline by the addition milk of lime, then heated and filtered : sulphuric acid must be added to neutralization, and on evaporation, crystals of tyros are deposited ; they may be purified in the manner already direct The formation of leucine appears to precede that of tyrosine, but when prepared by means of acids, and when the hydrated alkal are employed in effecting their production. This is readily accoun for when the composition of the two bodies is borne in mind:—

$$3\,(\overbrace{C_{12}H_{13}NO_4}^{\text{Leucine.}}) = 2\,(\overbrace{C_{18}H_{11}NO_6}^{\text{Tyrosine.}}) + H_3N + 14\,H.$$

Tyrosine appears also in certain cases to be a direct prod of the chemical actions in the living animal, since it was fou by De La Rue ready formed in the cochineal insect.

Tyrosine forms long fibrous crystals, which are very sparing soluble in cold water, and nearly insoluble in alcohol and ether boiling water dissolves it in considerable quantity. Although solutions are neutral to test paper, it is freely soluble both in and in alkaline solutions. When treated with hot nitric acid, yields oxalic acid; and if cold dilute nitric acid be employ *nitrate of nitrotyrosine* ($C_{18}H_{10}NO_4, NO_6, HO, NO_5$) is formed. very delicate test of the presence of tyrosine is afforded by formation of a red flocculent precipitate when its solution is mix with a nearly neutral solution of nitrate of the red oxide of mer cury, and if the solution be very dilute a rose-red colour is develop in the liquid (Reinhold Hoffmann). Tyrosine evidently belong to a class of compounds different from those homologous with gly cocine. It is a body which from the frequency of its occurren amongst the products of the decomposition of azotised matter merits a more complete examination than it has as yet received.

ammonia it constitutes almost the whole of the excrement of serpents, such as the boa. The beds of guano found in the rainless islands of the Pacific, which are formed of the accumulated excrements of countless generations of sea-fowl, consist chiefly of urate of ammonia, which has undergone decomposition more or less extensive. When uric acid is secreted in excess in man, it is often deposited from the urine in the form of hard crystalline grains, forming what is commonly termed red gravel; or it collects into larger masses which, if retained in the bladder, gradually acquire considerable size, and constitute the most usual variety of urinary calculus. In gouty patients also uric acid not unfrequently accumulates around the joints affected: and in combination, principally with soda, forms the white friable concretions often improperly called *chalk stones.*

Uric acid is best prepared from the dried urine of the boa by dissolving 1 part of the powdered mass in from 40 to 50 parts of boiling water, to which an excess of potash is added, sufficient to bring the whole of the acid into solution: during this operation ammonia escapes abundantly. The heat must be continued until the ammoniacal odour has disappeared. The brownish liquid thus procured contains an impure urate of potash, which must be filtered while hot, and decomposed by adding a slight excess of hydrochloric acid. Uric acid is immediately separated in minute white crystals; these must be washed with cold water, dissolved a second time in potash, and once more precipitated by hydrochloric acid; the product, after being thoroughly washed, and then dried, is quite pure. Uric acid crystallizes in rhombic tables, the outlines of which are frequently rounded; but when it is deposited from animal fluids the form of the crystals is often much modified. If a cold saturated solution of urate of potash be decomposed by hydrochloric acid, large crystals of the acid are obtained with 4 Aq. This water is expelled when the acid is heated to 212°.*

Pure uric acid is a white crystalline powder requiring 10,000 parts of cold water for solution, to which, however, it imparts a feeble acid reaction. Uric acid is insoluble in alcohol and in ether, but it is dissolved by concentrated sulphuric acid, and is deposited in a hydrated condition on diluting the solution. The urates of potash and of ammonia are more soluble than the free acid. The acid urates of ammonia, of soda, and of lime are

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* When uric acid is long boiled with a solution of potash, 6 equivalents of water are assimilated, and *uroxanate of potash* ($2\ KO, C_{10}H_8N_4O_{10}\ 6\ Aq$) is formed in small quantity. On the addition of a strong acid, uroxanic acid is separated in sparingly soluble microscopic tetrahedral crystals.

frequent ingredients of urinary calculi; the proportion of
salt, however, is always very small. The reaction of uric ac
nitric acid and ammonia is highly characteristic, and it
the acid to be detected in very minute quantities; the m
proceeding will be described under the head of murexid (1

(1383) *Urates.*—Uric acid is dibasic. Its salts ha
carefully examined by Bensch (Liebig's *Annal.*, liv. 189,
181). All the urates are but sparingly soluble in wate
are much more soluble in alkaline solutions, especiall
heated. They are also freely soluble in solutions of
Two urates of potash may be formed: the *acid* salt (K
$C_{10}H_2N_4O_4$) is the one best known. It is precipitate
granular form when carbonic acid is transmitted through
tion of the neutral salt. It is soluble in about 80 parts of
water, from which, on cooling, it is deposited in amorphous
it requires about 800 parts of cold water for solution. The
urate of potash ($2KO, C_{10}H_2N_4O_4$) is obtained by saturatin
dilute solution of potash, free from carbonate, with uric
pended in water, and boiling down the solution in a retort
certain degree of concentration the salt is deposited in fine a
needles: the clear liquid must be decanted from them,
must be washed with dilute alcohol. This salt requires
parts of cold water for solution, and 35 of boiling water.
tion is slowly decomposed by ebullition. This salt has
taste, and rapidly absorbs carbonic acid from the air.

There are two *urates of soda*, both of which ar
drous; they are each somewhat less soluble than th
sponding potash salts. The *acid urate of ammonia* (H_4N
$C_{10}H_2N_4O_4$) is the only urate of ammonia which is kno
usually forms a white amorphous mass, which is soluble
parts of cold, and 240 of boiling water; it is deposited
needles from a boiling aqueous solution of it, which con
excess of ammonia. Only the *acid urate of magnesia* (M
$C_{10}H_2N_4O_4, 6Aq$) is known; but both a neutral ($2CaO, C_{10}H_2N$
an acid urate of *lime* ($CaO, HO, C_{10}H_2N_4O_4, 2Aq$) may be o

(1384) *Products of the Decomposition of Uric Acid.*-

which it is altered by oxidizing agents, and the number of definite and crystallizable compounds to which it gives rise. These products were first investigated by Liebig and Wöhler (Liebig's *Annal.*, xxvi. 241). Such metamorphoses of animal products by oxidation always present a high physiological interest, inasmuch as the great changes which occur under the influence of vitality are changes in which oxidation plays the principal part. The oxidation of uric acid may be effected in various ways, such as by means of nitric acid, by peroxide of lead, by ferridcyanide of potassium mixed with caustic potash; the products of oxidation differing according to the nature of the agent employed.

The following table exhibits the most important of the derivatives of uric acid:—

Uric acid	$2\,HO,\ C_{10}H_2N_4O_4$	$= C_{10}H_4\,N_4O_6$
Uroxanic acid . . .	$2\,HO,\ C_{10}H_8N_4O_{10}$	$= C_{10}H_{10}N_4O_{12}$
Alloxan	$C_8\,H_2N_2O_8,\ 2\,Aq$	$= C_8\,H_2\,N_2O_8,\ 2\,Aq$
Dialuric acid	$HO,\ C_8\,H_3N_2O_7$	$= C_8\,H_4\,N_2O_8$
Alloxantin	$\left\{\begin{array}{l} C_8\,H_2N_2O_8, \\ +C_8H_3N_2O_7,\ 5Aq \end{array}\right\}$	$= C_{16}H_4\,N_4O_{14},\ 6Aq$ or $C_8\,H_2\,N_2O_7,\ 3Aq$
Alloxanic acid . . .	$2\,HO,\ C_8\,H_2N_2O_8$	$= C_8\,H_4\,N_2O_{10}$
Mykomelinic acid . .	$HO,\ C_8\,H_3N_4O_3,\ Aq$	$= C_8\,H_4\,N_4O_4.Aq$
Mesoxalic acid . . .	$2\,HO,\ C_6\quad O_8$	$= C_6\,H_2\,O_{10}$
Leucoturic acid . . .	$HO,\ C_6\,H_2N_2O_5$	$= C_6\,H_3\,N_2O_6$
Difluan	$C_6\,H_4N_2O_5$	$= C_6\,H_4\,N_2O_5$
Parabanic acid . . .	$2\,HO,\ C_6\quad N_2O_4$	$= C_6\,H_2\,N_2O_6$
Oxaluric acid	$HO,\ C_6\,H_3N_2O_7$	$= C_6\,H_4\,N_2O_8$
Uramil (dialuramide) .	$H_2N,\ C_8H_3N_2O_6$	$= C_8\,H_5\,N_3O_6$
Thionuric acid . . .	$2\,HO,\ C_8\,H_3N_3O_6,\ 2\,SO_2$	$= C_8\,H_5\,N_3O_{12}S_2$
Murexid		$= C_{24}H_{12}N_{10}O_{16}$?
Allantoin		$= C_8\,H_6\,N_4\,O_6$
Hidantoic acid . . .	$HO,\ C_8\,H_8N_4O_8$	$= C_8\,H_9\,N_4\,O_9$
Allanturic acid . . .	$HO,\ C_{10}H_6N_2O_8$	$= C_{10}H_7\,N_2\,O_9$
Lantanuric acid . . .	$HO,\ C_6\,H_4N_2O_6$	$= C_6\,H_5\,N_2\,O_7$.

Liebig and Wöhler have shown that when uric acid is submitted to the oxidizing action of dilute nitric acid it is converted into urea and alloxan:—

$$\overbrace{2\ HO,\ C_{10}H_2N_4O_4}^{\text{Uric Acid.}}+4\ HO+2\ O=\overbrace{C_8H_2N_2O_8,\ 2\ HO}^{\text{Alloxan.}}+\overbrace{C_2H_4N_2O_2}^{\text{Urea.}};$$

and if alloxan be boiled with an alkaline solution, it loses the whole of its nitrogen in the form of urea, whilst mesoxalic acid is formed:—

$$\overbrace{C_8H_2N_2O_8,\ 2\ HO}^{\text{Alloxan.}}+2\ HO=\overbrace{C_2H_4N_2O_2}^{\text{Urea.}}+\overbrace{2\ HO,\ C_6O_8}^{\text{Mesoxalic Acid.}}.$$

The urea is in these cases decomposed partially or entirely by the action of the acid or of the alkali upon it. Since the whole of the nitrogen of the uric acid is thus eliminated in the form of urea, which may be regarded as cyanate of ammonia, it may be inferred that the nitrogen is contained both in uric aci in alloxan, in two forms, one half of it being in the for derivative of cyanogen, the other half in that of a derivati ammonia. The remainder of the carbon and other compon ments of uric acid constitute mesoxalic acid. Liebig and W assume the existence of a radicle in uric acid, which they *uril* or *cyanoxalic acid* ($C_8N_2O_4 = C_4O_4Cy_2$)—a compound sponding to oxalic anhydride, in which two equivalents of ox have been displaced by two of cyanogen. This compound, h ever, has not been isolated, and the assumption of its exis appears unnecessary, since it does not materially aid in expl the changes which uric acid undergoes.

Alloxan is itself susceptible of various transformations, w give rise to several interesting compounds, of which the important are the following:—

Alloxanic Acid, which in its normal state is metameric with octohedral form of alloxan (1); ***Dialuric Acid***, which may be garded as a hydride of alloxan (2); ***Alloxantin***, or a compou alloxan with dialuric acid (3). If alloxan be treated with nitric it yields *Parabanic Acid* (4); and this acid, under the influ of bases, assimilates the elements of water, and is converted i *Oxaluric Acid* (5); whilst the solution of oxaluric acid, if boil also combines with water, and breaks up into oxalic acid and (6), as may be seen by the annexed equations:—

$$(1)\quad \overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}} + 2\,BaO = 2\,\overbrace{BaO,\,C_8H_2N_2O_8}^{\text{Alloxanate of Baryta.}}.$$

$$(2)\quad \overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}} + \overbrace{H_4NS,HS}^{\text{Hydrosulph. Ammon.}} = \overbrace{H_4NO,C_8H_3N_2O_7}^{\text{Dialurate of Ammonia.}} + S_2.$$

$$(3)\quad \overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}} + \overbrace{HO,C_8H_3N_2O_7}^{\text{Dialuric Acid.}} + 4\,HO = \overbrace{C_{16}H_4N_4O_{14}.\,6\,HO}^{\text{Alloxantin.}}$$

$$(4)\quad \overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}} + O_2 = \overbrace{2\,HO,\,C_6N_2O_4}^{\text{Parabanic Acid.}} + 2\,CO_2.$$

$$(5)\quad \overbrace{2\,HO,\,C_6N_2O_4}^{\text{Parabanic Acid.}} + H_3N + 2\,HO = \overbrace{H_4NO,\,C_6H_3N_2O_7}^{\text{Oxalurate of Ammonia.}}.$$

$$(6)\quad \overbrace{HO,\,C_6H_3N_2O_7}^{\text{Oxaluric Acid.}} + 2\,HO = \overbrace{2\,HO,\,C_4O_6}^{\text{Oxalic Acid.}} + \overbrace{C_2H_4N_2O_2}^{\text{Urea.}}.$$

(1385) *Alloxan* ($C_8H_2N_2O_8$ + 2 and 8 Aq), is best obtained by adding to nitric acid (of sp. gr. 1·42) pure uric acid in small portions at a time, waiting till the effervescence produced by the addition of each separate quantity h [illegible] led, and taking care to moderate the heat generated by the reaction, by immersing the vessel in cold water if necessary. The temperature must not be allowed to rise much above 120°. During this operation, carbonic acid and nitrogen escape abundantly. Uric acid must be added until crystals begin to be formed; the liquid must then be allowed to cool, when an abundant deposit of octohedral crystals of alloxan will occur. These crystals must be drained in a funnel partially obstructed with asbestus, washed with ice-cold water, and dried on a tile. In this form alloxan was regarded as anhydrous by Liebig and Wöhler, but later researches appear to show that it must be regarded as containing two equivalents of water, since Gmelin finds that if it be heated to from 300° to 320° it loses 11·3 per cent. or two equivalents of water. If these octohedral crystals be redissolved in water at 120° they yield on evaporation transparent prisms containing eight equivalents of water. The changes which attend the formation of alloxan from uric acid by the action of nitric acid, may be thus represented in two consecutive stages, though the decompositions appear to occur simultaneously:—

$$(1)\ \overbrace{2HO,C_{10}H_2N_4O_4}^{\text{Uric Acid.}} + HO + HO,NO_5 = \overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}} + \overbrace{C_2H_4N_2O_2}^{\text{Urea.}} + NO_3.$$

But, since urea and nitrous acid immediately decompose each other, nitrogen and carbonic acid are disengaged with effervescence, whilst water and ammonia are found in the liquid with the alloxan:—

$$(2)\ \overbrace{C_2H_4N_2O_2}^{\text{Urea.}} + NO_3 = 2\,CO_2 + H_3N + N_2 + HO.$$

Alloxan may also be prepared by mixing four parts of uric acid with eight of commercial hydrochloric acid, and gradually adding one part of powdered chlorate of potash. Under these circumstances no effervescence occurs, and the whole of the urea is found in solution. The temperature must be carefully prevented from rising too high.

Alloxan is freely soluble in water; it stains the skin pink, and gives it a sickly odour, and, though not possessed of acid properties, it reddens litmus paper. Although it is a stable and definite substance, when once formed, yet it is readily transformed into other products. When alloxan is boiled with peroxide of lead it yields urea and carbonic acid, the peroxide of lead being converted into protoxide:—

$$\overbrace{C_8H_2N_2O_8,\ 2\,HO}^{\text{Alloxan.}} + 4\,PbO_2 = \overbrace{C_2H_4N_2O_2}^{\text{Urea.}} + 6\,CO_2 + 4\,PbO.$$

A characteristic property of alloxan is the formation of an intensely violet purple-coloured liquid on admixture with solution of a protosalt of iron. Long-continued boiling decom solution of alloxan, carbonic acid is given off, and the contains a mixture of parabanic acid and alloxantin:—

$$\underbrace{3(C_8H_2N_2O_8, 2\,HO)}_{\text{Alloxan.}} = \underbrace{(C_{16}H_4N_4O_{14}, 6\,HO)}_{\text{Alloxantin.}} + \underbrace{2\,HO, C_6N_2O_4}_{\text{Parabanic Acid.}} +$$

(1386) *Alloxanic Acid* (2 HO, $C_8H_2N_2O_8$).—By treating with baryta water, so long as the precipitate produced is re on agitation, and gently heating the mixture, two equiva water are displaced by the baryta, and a salt is formed crystallizes as the liquid cools. This compound contains *acid*, which may be separated by the cautious addition of ric acid, and may be obtained in crystals by evaporation.[*]

A solution of alloxan in ammonia is nearly colourless heated gently it becomes yellow, and on cooling forms a transparent gelatinous mass of *mykomelate of ammonia*, liquid retains urea in solution, with alloxanate and mesox ammonia; these are probably the results of secondary Mykomelinic Acid contains the elements of 1 equivalent of and 2 of ammonia, from which 4 equivalents of water have separated:—

$$\underbrace{C_8H_2N_2O_8}_{\text{Alloxan.}} + 2\,H_3N = \underbrace{HO, C_8H_3N_4O_3}_{\text{Mykomelinic Acid.}} + 4\,HO.$$

If alloxanic acid be neutralized by ammonia it gives nitrate of silver a white precipitate, which, by boiling, first bec yellow, and is afterwards reduced with effervescence.

(1387) *Mesoxalic Acid* (2 HO, C_6O_8).—When alloxanate baryta is subjected to prolonged boiling it is decomposed; am liberated, and a yellowish precipitate is formed, consisting of mixture of carbonate of baryta and a sparingly soluble mesox of baryta, the carbonate of baryta being the result of secondary decomposition of the urea. The following equat

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[*] Alloxanic acid is an unstable compound. If its aqueous solution be boiled, carbonic acid is emitted; and if the solution be rapidly reduced to the consistence of a syrup, and then diluted with water, it is only partially dissolved; the insoluble portion is named by Schlieper (Liebig's *Annal.*, lvi. 1) *leucoturic acid* (HO, $C_6H_2N_2O_5$); the solution contains a white deliquescent body, termed *difluan* ($C_6H_4N_2O_5$). Nitric acid reconverts the latter into alloxan, and potash decomposes it with evolution of ammonia and formation of oxalic acid. The formation of these bodies from alloxanic acid may be thus indicated:—

$$\underbrace{2\,(2\,HO, C_8H_2N_2O_8)}_{\text{Alloxanic Acid.}} = \underbrace{HO, C_6H_2N_2O_5}_{\text{Leucoturic Acid.}} + \underbrace{C_6H_4N_2O_5}_{\text{Difluan.}} + 4\,CO_2 + HO.$$

shows the process of the transformation of alloxanic into mesoxalic acid :—

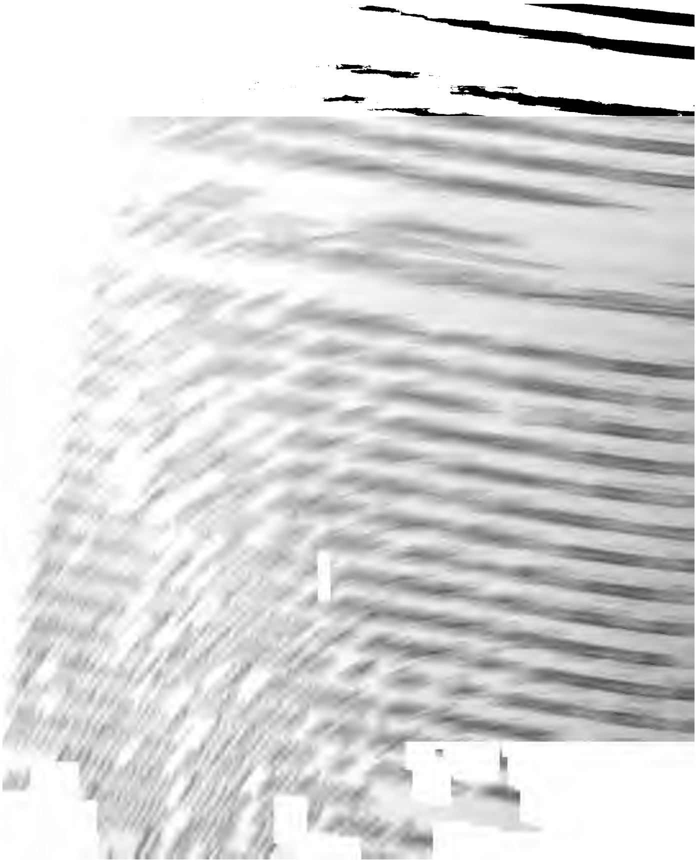
$$\overbrace{2\,BaO,\ C_8H_2N_2O_8}^{\text{Alloxanate of Baryta.}} + 2\,HO = \overbrace{2\,BaO,\ C_6O_8}^{\text{Mesoxalate of Baryta.}} + \overbrace{C_2H_4N_2O_2}^{\text{Urea.}}.$$

Mesoxalic acid may be procured in a free state by the addition of sulphuric acid to the baryta salt, the solution when evaporated yields crystals, which are very soluble in water; it is powerfully acid, and has a very sour taste. The most characteristic reaction of mesoxalic acid is the formation of a yellow precipitate of mesoxalate of silver, when a solution of mesoxalate of ammonia is mixed with one of nitrate of silver: this precipitate when heated is decomposed with a brisk effervescence, owing to the escape of carbonic acid and carbonic oxide, whilst metallic silver is left; $2\,AgO,\ C_6O_8 = 2\,Ag + 4\,CO_2 + 2\,CO$. When to a boiling solution of alloxan a boiling solution of acetate of lead is added, a yellow, heavy, insoluble precipitate of mesoxalate of lead is formed, from which the acid may be obtained by decomposing the precipitate by means of sulphuretted hydrogen.

(1388) *Parabanic Acid* ($2\,HO,\ C_6N_2O_4$) is formed by concentrating the acid mother liquor of alloxan, till on cooling it forms a soft crystalline mass; $C_8H_2N_2O_8 + NO_5 = 2\,HO,\ C_6N_2O_4 + 2\,CO_2 + NO_3$. This is to be dried on a tile, redissolved in water, and recrystallised, when it forms thin, colourless, six-sided prisms: it is a powerful acid, very permanent in its uncombined condition, and very soluble in water. At a heat of 212° it acquires a reddish tint: at a higher temperature it undergoes partial sublimation, but a portion of it is decomposed, and furnishes hydrocyanic acid. Parabanic acid forms salts which are exceedingly unstable; parabanate of silver being the only salt which is permanent. All the other parabanates during evaporation combine with two equivalents of water, and become converted into oxalurates: parabanate of ammonia, for instance, when boiled furnishes brilliant crystals of oxalurate of ammonia :—

$$\overbrace{HO,\ H_4NO,\ C_6N_2O_4}^{\text{Parabanate of Ammonia.}} + 2\,HO = \overbrace{H_4NO,\ C_6H_3N_2O_7}^{\text{Oxalurate of Ammonia.}}.$$

(1389) *Oxaluric Acid* ($HO,\ C_6H_3N_2O_7$).—This acid is interesting from the circumstance of its being occasionally met with in urinary sediments, forming the dumb-bell crystals that were at first mistaken for oxalate of lime. Oxalurate of ammonia may be employed in preparing the acid; a hot saturated solution when



water, when added to its solution, gives a characteristic violet precipitate, which becomes white if boiled in the liquid. A solution of alloxantin reduces the salts of silver, and is converted into alloxan; thus affording an instance of the facility with which oxidizing agents reconvert it into alloxan. If a boiling solution of alloxantin be mixed with a solution of muriate of ammonia, also at a boiling temperature, and the mixture be allowed to cool in a well-corked vessel, crystals of *uramil* (dialuramide) are deposited, whilst the liquid retains alloxan and free hydrochloric acid in solution:—

$$\overbrace{C_{16}H_4N_4O_{14}}^{\text{Alloxantin.}} + H_4N,Cl = \overbrace{C_8H_5N_3O_6}^{\text{Uramil.}} + HCl + \overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}}.$$

When alloxan is boiled with hydrochloric acid it is gradually decomposed, alloxan and parabanic acid are formed, accompanied by two compounds, termed by Schlieper *allituric* acid ($C_6H_3N_2O_4$) and *dilituric* acid. The last named acid has not been analysed in its uncombined form.

(1391) *Dialuric Acid* ($HO, C_8H_3N_2O_7$).—If a stream of sulphuretted hydrogen be transmitted in excess through a hot solution of alloxan or of alloxantin, sulphur is deposited, and the liquid becomes strongly acid, owing to the formation of *dialuric acid*. If this acid liquid be neutralized with ammonia, dialurate of ammonia is deposited in silky needles ($H_4NO, C_8H_3N_2O_7$). The same salt may be obtained by reducing alloxan by means of zinc and hydrochloric acid, and adding a sufficient excess of ammonia to redissolve the oxide of zinc, which is at first precipitated by the ammonia. If dialurate of ammonia be added to hot hydrochloric acid, so long as it is dissolved, and the liquid be allowed to cool, long needles of dialuric acid are deposited. They become red by exposure to the air, and are gradually converted into alloxantin. Dialuric acid forms a sparingly soluble salt with *potash*. It may be obtained by adding a solution of cyanide of potassium to one of alloxan. The brown yellow precipitate thus obtained must be dissolved in a weak potash ley, and neutralized by acetic acid, when it falls as a white precipitate. The dialurate of *ammonia* is white at the moment of its formation, but as it dries it becomes of a splendid pink or blood-red colour. This salt is freely soluble in boiling water. It occasions a white precipitate with the salts of baryta, and a yellow one with salts of lead. Nitrate of silver is reduced by it to the metallic state.

(1392) *Uramil*, or *Dialuramide* ($C_8H_5N_3O_6 = H_2N, C_8H_3N_2O_6$).

—This compound may be obtained by decomposing thi ammonia by boiling it for a few minutes with an acid:—

$$\overbrace{2\,H_4NO, C_8H_3N_3O_6, 2\,SO_2}^{\text{Thionurate of Ammonia.}} + 2\,HCl + 2\,HO =$$

$$2\,(H_4N,Cl) + 2\,(HO, SO_3) + \overbrace{C_8H_5N_3O_6}^{\text{Uramil.}}$$

It may also be procured by mixing boiling solutions of all and muriate of ammonia, freed from air (1390). Uramil cryst in penniform groups of brilliant hard needles, which are insol cold water, and sparingly soluble even in boiling water. W exposed to an atmosphere containing traces of ammo acquires a rose tint. Uramil is freely soluble in dilute alk solutions at ordinary temperatures, and is deposited from th unaltered on adding an acid. But if its solution in am be boiled, it gradually acquires a rich purple colour, and cooling deposits crystals of *murexid*:—

$$H_3N + 3\,\overbrace{(C_8H_5N_3O_6)}^{\text{Uramil.}} + O_4 = \overbrace{C_{24}H_{12}N_{10}O_{16}}^{\text{Murexid.}} + 6\,HO$$

If uramil be boiled for some time with oxide of mercury or silver a similar change occurs; the metallic oxide is reduced, and the liquid be filtered while hot, beautiful crystals of pure mure are deposited. An excess of the metallic oxide must be caref avoided, otherwise the purple colour disappears, and alloxan ammonia is formed in the liquid. A solution of uramil in pota evolves ammonia when heated; at ordinary temperatures it slow absorbs oxygen from the air, acquiring a fine purple colour, and depositing crystals of purpurate of potash; the liquid beco neutral, and contains alloxanate and mesoxalate of potash.

(1393) *Thionuric Acid* ($2HO, C_8H_3N_3O_6, 2\,SO_2$).—If a aqueous solution of alloxan be added to a solution of sulphit ammonia containing a considerable quantity of free ammonia, and the mixture be boiled for a few minutes, the ammonia and sul phurous acid unite with the elements of alloxan. As the liq cools, a beautiful salt, termed *thionurate of ammonia*, is deposited:—

$$\overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}} + 2\,SO_2 + 3\,H_3N = \overbrace{2\,H_4NO, C_8H_3N_3O_6, 2\,SO}^{\text{Thionurate of Ammonia.}}$$

By adding a solution of acetate of lead to the solution of this sa an insoluble gelatinous thionurate of lead is procured, which standing becomes converted into concentric groups of delica needles. This precipitate, on being decomposed by sulphurett hydrogen, gives pure thionuric acid, which may be obtained evaporation at a gentle heat, crystallized in slender needles. Its aqueous solution may be preserved unchanged at ordinary temperatures, but it undergoes decomposition when boiled; sulphuric acid being formed, whilst silky crystals of uramil are deposited. The thionurate of ammonia gives a pale yellowish brown precipitate with salts of copper. It gives no precipitate in acid solutions with salts of baryta, but a white one in neutral solutions: when mixed with nitrate of silver the metal is gradually reduced, and forms a mirror-like coating on the sides of the vessel.

(1394) *Murexid*, or *Purpurate of Ammonia* ($C_{24}H_{12}N_{10}O_{16}$?)—There are various modes of forming this beautiful compound. The decomposition of uramil by ammonia under the influence of oxygen, and by the action of oxide of mercury, have been already mentioned (1392). Another advantageous method of preparing murexid consists in adding alloxan to an ammoniacal solution of uramil. If the formula given for murexid be correct, this reaction must be attended with the absorption of oxygen:—

$$\overbrace{3\,(C_8H_5N_3O_6)}^{\text{Uramil.}} + 5\,H_3N + 2\,O + \overbrace{3\,(C_8H_2N_2O_8)}^{\text{Alloxan.}} = \overbrace{2\,(C_{24}H_{12}N_{10}O_{16})}^{\text{Murexid.}} + 12\,HO.$$

Murexid may also be obtained by adding a solution of carbonate of ammonia, drop by drop, to a boiling solution of alloxan, until the liquid has a slight ammoniacal odour; the solution then acquires a beautiful purple tint, becomes turbid, and on cooling deposits crystals of murexid. Murexid may also be prepared on a small scale by dissolving 4 grains of alloxantin and 7 of hydrated alloxan, in half an ounce of boiling water, and mixing the solution whilst hot with 80 grains of a cold saturated solution of carbonate of ammonia; brisk effervescence ensues, and a splendid purple liquid is produced, which on cooling deposits magnificent green crystals of murexid, with a golden lustre. These crystals, when heated to 212°, lose water to the extent of 3 or 4 per cent. Its brilliant colour is speedily destroyed by sulphuretted hydrogen, as well as by free ammonia. Murexid is but sparingly soluble in cold water, to which, however, it communicates its intense purple colour; hot water takes it up more freely.

When the solution of murexid is mixed with salts of lead, of baryta, and of silver, it yields purple precipitates. Dilute acids decompose the crystals of murexid, and cause the separation of scales of a sparingly soluble yellowish substance, termed *murexan*, which, in all probability, is an impure form of uramil; the solution contains a mixture of alloxan and alloxantin.

Murexid is a body resembling an amide in composition. The exact composition of this compound is not accurately established, but the formula above given agrees with the analyses of Liebig and Wöhler. Fritsche, from his experiments, represents its composition by the somewhat improbable formula ($C_{16}H_8N_6O_{11}$), which does not explain the mode of the formation of murexid.

Test for Uric Acid.—Advantage is taken of the formation of murexid, in order to detect very minute quantities of uric acid by the action of nitric acid. In applying this test, the substance supposed to contain uric acid is heated on a slip of glass with a drop of nitric acid, and evaporated cautiously to dryness. If uric acid be present, the residue has a red colour, which is converted by exposure to the vapour of ammonia into a fine crimson, and the addition of a drop of a solution of potash developes a splendid purple colour, which disappears on the application of heat, with extrication of ammonia.

(1395) *Allantoin* ($C_4H_3N_2O_3$ or $C_8H_6N_4O_6$).—This is a body which occurs in the allantoic fluid of the cow, or in the urine of the fœtal calf, but it may also be procured by the oxidation of uric acid. For this purpose, 1 part of uric acid must be suspended in 20 parts of water, and raised to the boiling point; finely levigated peroxide of lead is then to be added in small quantities at a time to the boiling liquid, until the oxide ceases to change colour. The peroxide of lead is reduced to the state of protoxide, and a brisk effervescence occurs, owing to the escape of carbonic acid, whilst oxalic acid is precipitated in combination with protoxide of lead; the supernatant liquid is colourless, and on filtering it and allowing it to cool, hard brilliant prismatic crystals of allantoin are deposited. Upon further concentration of the solution, fresh crystals of allantoin are obtained, and when the mother liquid has been evaporated until it acquires a syrupy consistence, crystals of urea are deposited. The reaction which attends the formation of allantoin is not well understood, and the equations hitherto given do not satisfactorily account for all the products. Liebig and Wöhler consider the reaction to be as follows (doubling the proportions given by these chemists to allow of doubling the equivalent of allantoin):—

$$\overbrace{2\,(2\,HO,C_{10}H_2N_4O_4)}^{\text{Uric Acid.}} + 4\,PbO_2 + 6\,HO = \overbrace{2\,(2PbO,C_4O_6)}^{\text{Oxalate of Lead.}}$$

$$+ \overbrace{C_8H_6N_4O_6}^{\text{Allantoin.}} + \overbrace{2\,(C_2H_4N_2O_2)}^{\text{Urea.}}.$$

The carbonic acid arises probably from the oxidizing action of the peroxide of lead upon the oxalate at the moment of its formation. Pelouze has however shown that the decomposition is in reality more complicated than it appears to be from the foregoing equation.

Allantoin is a neutral, tasteless substance, sparingly soluble in cold water, but freely soluble in boiling water. It shows but small tendency to combine with other bodies; but a compound of allantoin with oxide of silver may be obtained by mixing a boiling solution of allantoin with one of nitrate of silver, and adding ammonia drop by drop; a white precipitate ($C_8H_5AgN_4O_6$) is thus occasioned. It is probable, therefore, that the usually received equivalent of allantoin should be doubled. When allantoin is boiled with solutions of the alkalies, it undergoes decomposition, ammonia being evolved whilst oxalic acid is formed:—

$$\overbrace{C_8H_6N_4O_6}^{\text{Allantoin.}}+2\,HO+4\,(KO, HO)=4\,H_3N+2\,(\overbrace{2\,KO, C_4O_6}^{\text{Oxalate of Potash.}}).$$

Allantoin is readily decomposed by simple elevation of temperature: when its aqueous solution is heated in a closed tube to about 280° F. it is resolved into a new acid, *allanturic acid* ($HO, C_{10}H_6N_4O_8$; Pelouze), and into carbonate of ammonia; both these substances being produced from the elements of allantoin by the assimilation of the elements of water:—

$$3\overbrace{(C_8H_6N_4O_6)}^{\text{Allantoin.}}+12\,HO=2\overbrace{(HO, C_{10}H_6N_4O_8)}^{\text{Allanturic Acid.}}+4\overbrace{(H_4NO, CO_2)}^{\text{Carbonate of Ammonia.}}.$$

Allantoin also assimilates water and is transformed into allanturic acid by heating it gently with nitric acid, or with hydrochloric acid, and urea is at the same time formed:—

$$3\,\overbrace{(C_8H_6N_4O_6)}^{\text{Allantoin.}}+4\,HO=2\,\overbrace{(HO, C_{10}H_6N_4O_8)}^{\text{Allanturic Acid.}}+2\,\overbrace{(C_2H_4N_2O_2)}^{\text{Urea.}}.$$

Pelouze considers that the urea found in the mother liquors, obtained during the preparation of allantoin from uric acid by means of peroxide of lead, is due to this secondary action; this, however, is very doubtful.

Allanturic acid is a white deliquescent substance, which gives white precipitates with nitrate of silver and with the acetates of lead; these precipitates are soluble in an excess of these salts, as well as in free allanturic acid.

When allantoin is digested for some days with a concentrated solution of potash, then mixed with acetic acid in excess, and treated with a solution of acetate of lead, an insoluble lead salt of a new acid, termed *hidantoic acid* ($HO, C_8H_8N_4O_8$? Schlieper), is formed. The normal acid contains the elements of two equivalents of allantoin with three additional equivalents of water. Its anhydride is polymeric with oxamide.

Lantanuric Acid ($HO, C_6H_4N_2O_6$?) is the name given by Schlieper to a result obtained by adding the powdered uric acid to a solution of ferridcyanide of potassium and hydrate of potash at ordinary temperatures. Under these circumstances the red prussiate is rapidly converted into the yellow prussiate of potash, whilst oxygen is liberated, which, in its nascent condition, attacks the uric acid; $K_3, Fe_2Cy_6 + KO = 2\,(K_2, FeCy_3) + O$. Allantoin and carbonic acid are first produced,—

$$\overbrace{2\,HO, C_{10}H_2N_4O_4}^{\text{Uric Acid.}} + O_2 + 2\,HO = \overbrace{C_8H_6N_4O_6}^{\text{Allantoin.}} + 2\,CO_2,$$

and the allantoin combining with an additional quantity of water is resolved into lantanuric acid and urea:—

$$\overbrace{C_8H_6N_4O_6}^{\text{Allantoin.}} + 3\,HO = \overbrace{HO, C_6H_4N_2O_6}^{\text{Lantanuric Acid.}} + \overbrace{C_2H_4N_2O_2}^{\text{Urea.}}.$$

It is possible that lantanuric acid may be identical with the allanturic acid of Pelouze: it is a deliquescent substance, which forms a white insoluble salt with oxide of lead, and its properties agree very closely with those ascribed by Pelouze to allanturic acid, respecting the analysis of which no details have hitherto been published.

(1396) A few other substances will now be noticed which exhibit some relation, either in their composition or their origin, to uric acid; viz.:—

Xanthic oxide	$C_{10}H_4N_4O_4$
Hypoxanthin	$C_{10}H_4N_4O_2$
Guanine	$C_{10}H_5N_5O_2$
Cystin	$C_6\,H_6NO_4S_2$.

Xanthic or *Uric Oxide* ($C_{10}H_4N_4O_4$) was discovered by Dr. Marcet as the principal constituent of a very rare variety of urinary calculus. Göbel has since found it in some oriental bezoars extracted from the intestines of certain ruminating animals. The concretions which contain xanthic oxide are of a pale brown colour; they have a polished surface, and a lamellar fracture. These calculi are readily soluble in a solution of potash; and on neutralizing the alkaline solution with an acid, xanthic oxide is precipitated in the form of a white powder, which is insoluble in water, alcohol, and ether. It acquires a waxy lustre on friction with a hard body. Hydrochloric acid does not dissolve it, but it is soluble in nitric acid without effervescence: the solution, when evaporated, leaves a lemon-coloured residue (hence the name *xanthic*, from ξανθὸς yellow). This residue does not become red by the action of ammonia. When distilled, xanthic oxide yields hydrocyanic acid and carbonate of ammonia, but no urea. It contains two equivalents of oxygen less than normal uric acid. *Hypoxanthin* ($C_{10}H_4N_4O_2$) contains two equivalents of oxygen less than the preceding compound. It was found by Scherer in the liquid contained in the substance of the spleen both of man and of the cow. Hypoxanthin is a white powder, which is nearly insoluble in water, but soluble in a dilute solution of potash; it is attacked by nitric acid with evolution of gas, and leaves a crystalline residue.

Guanine ($C_{10}H_5N_5O_2$) was obtained by Unger from guano; it is also found to constitute the principal portion of the excrement of the garden spider (*Epeira diadema*). In order to obtain it from guano, this substance must be boiled with milk of lime until the liquid shall have acquired a yellowish-green tint instead of a brown colour. The liquid must then be filtered and neutralized with hydrochloric acid. The guanine is slowly deposited, mixed with uric acid, and assumes the form of a flesh-coloured precipitate. This precipitate, when boiled with hydrochloric acid, gives up the guanine, and on cooling, a compound of this body with hydrochloric acid is obtained in crystals: the acid may be removed by digestion with ammonia. Certain specimens of guano were found to yield nearly 6 per cent. of this substance. Guanine forms a yellow powder which is insoluble in water, alcohol, and ether. It appears to possess the properties of a feeble base, and is soluble in hot dilute acids, forming unstable compounds with them. Guanine forms both neutral and acid salts, the neutral compound with hydrochloric acid being $[3\ (C_{10}H_5N_5O_2,\ HCl),\ 7\ Aq]$, and the acid salt $(C_{10}H_5N_5O_2,\ 2\ HCl)$; both of them lose the whole of the acid on being heated to 392°. Other salts of guanine contain three equivalents of the base and four of acid. Guanine forms a crystallizable double chloride with bichloride of platinum $(C_{10}H_5N_5O_2,\ HCl,\ 2\ PtCl_2,\ 4\ Aq)$. Guanine also combines with the alkalies, and is more soluble in alkaline solutions than in the acids. It is readily oxidized by a mixture of chlorate of potash and hydrochloric acid, yielding oxalate of ammonia and a small quantity of a crystalline compound ($C_{10}H_5N_4O_9$), named *peruric* acid by Unger. This substance is colourless and tasteless, and crystallizes in tufts of rhombic prisms.

Cystin, or *Cystic Oxide* ($C_6H_6NO_4S_2$).—This substance constitutes a rare form of urinary calculus. Calculi composed of it are semi-transparent and of a brownish-yellow colour, and crystalline texture. Cystin is insoluble in water, alcohol, and ether, but it is dissolved by the stronger acids, such as the sulphuric, nitric, hydrochloric, and phosphoric. It is also freely soluble in alkaline solutions, whether caustic or carbonated, from which it can be precipitated by the addition of an acid such as the acetic. It may readily be obtained crystallized in hexagonal plates by allowing its ammoniacal solution to evaporate spontaneously. When heated it does not melt, but is decomposed, emitting a peculiar fœtid odour. Cystin contains 25·5 per cent. of sulphur.

Kynurenic Acid is the name given by Liebig to a peculiar acid found in the urine of the dog. It forms very light, silky, colourless, delicate needles, which are soluble in alkaline solutions, nearly insoluble in water, and insoluble in alcohol and ether. It is soluble in hot dilute acid solutions, and is deposited from them on cooling. It combines with the alkalies, forming soluble crystalline salts. Kynurenic acid does not appear to contain nitrogen. Its composition has not been ascertained. When heated in a small tube it yields a crystalline sublimate, and leaves scarcely a trace of any carbonaceous residue.

CHAPTER XI.

ALBUMINOID AND GELATIGENOUS PRINCIPLES.

(1397) THE greater number of the compounds of organic chemistry which have hitherto occupied our attention, are destitute of organic structure; they contain in each of their constituent or equivalent molecules only a moderate number of elementary atoms, in which respect they differ from the compounds which remain to be described, since these are of a much more complex character. These bodies enter into the formation of the organized textures, and are destitute of crystalline character. The most important of these substances, viz., fibrin and albumen, occur both in plants and in animals. The proportion of these compounds in the solid and liquid components of the organs of plants is but small, but they are never entirely wanting in some portion or other of their organism. They are most abundant in the seed. These substances abound, however, in the animal tissues, and constitute their most remarkable and distinctive ingredients. Owing to the complexity of their composition no satisfactory rational formula can at present be assigned to any of these azotised bodies; and, owing to their indisposition to crystallize, great difficulty is experienced in obtaining them in a state of purity, and of ascertaining when they are really free from foreign admixture. All of them contain sulphur amongst their components, though the proportion of this element never exceeds 2 per cent.

These azotised compounds may be subdivided into two groups: of these the more important is termed the *proteic* or the *albuminoid* group, owing to the general resemblance of its members to albumen or white of egg; it comprises albumen, fibrin, casein, and legumin, in which the proportion of carbon to nitrogen is that of eight equivalents of the former to one of the latter. The second group is the *gelatigenous*: it comprises gelatin, chondrin, and ossein.

(1398) *Products of the Oxidation of the Proteic and Gelatigenous Groups.*—When these azotised substances are submitted to the gradual action of oxidizing agents, they furnish a great variety of products, which, however, belong to the three principal groups; viz., to the acetic, the benzoic, and the cyanic series. Amongst the volatile products furnished by treating albuminoid substances with a mixture of bichromate of potash and sulphuric acid, or with a mixture of peroxide of manganese and sulphuric acid, Guckelberger (Liebig's *Annal.*, lxiv. 39) obtained the following products, besides others which have not been specially identified:—

Formic acid
Acetic acid
Propionic acid
Butyric acid
Valeric acid
Caproic acid.

Acetic aldehyd
Propionic aldehyd
Butyric aldehyd.

——

Benzoic acid
Hydride of benzoyl.

——

Hydrocyanic acid
Valeronitrile.

The volatile products of oxidation are the only ones which have as yet been fully examined. The most abundant of these products are the series of volatile acids: next to these the products of the benzoic series occur in the largest quantity, whilst the hydrocyanic is obtained in the smallest quantity. The proportion in which these substances are formed varies according as casein, fibrin, albumen, or gelatin has been the body submitted to oxidation.

Gelatin yields the largest quantity of formic, acetic, and valeric acids (Schlieper, Liebig's *Annal.*, lix. 1). Fibrin gives the largest proportion of butyric acid, and casein yields the compounds of benzoyl in greatest abundance. There can be no doubt that these bodies originate in more complex organic products, which are the first results of the breaking up of these complicated azotised substances. Thus leucine and tyrosine are amongst the products obtained in an early stage of the reaction, and they break up into valeric acid, ammonia, and probably other compounds. When the proteic and gelatigenous substances are fused with hydrate of potash they yield leucine and tyrosine, together with variable quantities of acetate, valerate, and other salts of potash, which belong to the series of fatty acids.

(1399) *Formation of Urea from Albuminoid bodies.*—According to Béchamp (*Ann. de Chimie,* III. xlviii. 352), urea may be obtained in the following manner by the oxidation of albuminoid substances:—Ten parts of the albuminoid body (supposed to be freed from moisture) are to be diffused through 300 parts of water, and 75 parts of permanganate of potash to be gradually added. A rapid reduction of the permanganate commences at ordinary temperatures; by degrees the temperature must be raised to about 110°, and very dilute sulphuric acid must be added cautiously, so that the excess of alkali shall be neutralized as it is formed, taking care, however, that the liquid shall always preserve a slight degree of alkalinity. As soon as the colour of the permanganate has disappeared, the liquid is to be filtered and accurately neutralized by the addition of sulphuric acid. It must then be evaporated on a water-bath, and the syrupy residue thus obtained treated with strong alcohol; the alcoholic liquid is next to be decanted from the sulphates of potash and ammonia, concentrated till it acquires the consistence of honey, and then treated with absolute alcohol, which dissolves the urea. In the first stage of this oxidation the liquid acquires a gelatinous consistence, but it again speedily becomes liquid. An azotised acid, the nature of which has not been ascertained, is formed in the earlier part of the process; neither acetic nor valeric acid is produced, and if the operation be conducted with due care, no gas is liberated. A portion of the nitrogen is found in the liquid in the form of ammonia, as well as in that of urea. If the excess of alkali be not neutralized as the operation proceeds, a higher temperature is necessary to effect the oxidation, and but little urea is formed, since it undergoes decomposition at the moment of its formation. Care must also be taken to avoid the presence of an excess of the permanganate, otherwise the whole of the nitrogen appears in the form of ammonia. The fibrin of the blood appears to furnish urea more readily than either albumen or gluten.

§ I. The Proteic or Albuminoid Group.

(1400) It has been already stated that the more important members of this group are albumen, fibrin, casein, and legumin, but it comprises several modifications of these bodies of minor importance, such as globulin and vitellin. The different forms of mucus also exhibit a close relationship to the compounds of this division.

Albumen is the characteristic ingredient of white of egg, and of the serous portion of the blood. *Fibrin* is the principal constituent of muscular tissue, and is that component of the blood which occasions its spontaneous coagulation; *casein* is that constituent of milk which is separated in the form of curd on the addition of an acid; it is the essential component of cheese. *Legumin* is abundant in the seeds of the leguminous plants, such as peas, beans, and lentils. Liebig regards legumin as identical with casein; but many other chemists consider that it has hitherto been found only in the vegetable kingdom, and casein only in the animal: albumen and fibrin are, however, generally admitted to occur in both divisions of the organic creation. No animal can continue to subsist upon food in which these azotised substances are entirely wanting. This circumstance is explained by the important observations of Liebig, who first clearly insisted upon the fact that none of these proteic principles are ever produced by the animal organism: they are elaborated in the growing plant, and are merely assimilated by the animal in the process of digestion. The proteic principles furnish those essential ingredients of the blood which are concerned in repairing the soft azotised portions of the body, such as the muscular and nervous tissues, as they become effete: hence the proteic principles have been termed the *plastic* materials of nutrition, in order to distinguish them from other portions of the food which, like starch and fatty matters, are especially needed for maintaining the function of respiration, and which have been termed the *respiratory* materials of the food. It will, however, be necessary to consider the components of food more in detail (1457) after the properties of the albuminoid principles have been discussed.

The albuminoid principles may be preserved in a dry state for an indefinite period without change, but if exposed to the air while moist, they gradually putrefy and emit a sickening odour. According to Lehmann, among the products of putrefaction are always to be found carbonate, butyrate, valerate, and hydrosulphate of ammonia, together with leucine and tyrosine. The readiness with which the albuminoid bodies putrefy and undergo spontaneous chemical changes when moist is one of their most striking characters. Synaptase, diastase, pepsin, and other ferments are considered by Liebig to be modifications of albumen in particular states of decay; and yeast itself, although an organized structure, is supposed to owe a part of its remarkable power of exciting fermentation, to the presence of azotised matter, which is undergoing definite transformation, although the nature of the change is but little understood. If albuminoid matters be heated in close vessels, they first swell up and fuse, then blacken, and emit a large quantity of fœtid empyreumatic products, among which ammonia and sulphuretted hydrogen are always present; and they leave in the retort a porous, brilliant, carbonaceous mass. When incinerated they leave a notable amount of ash: this varies in quantity in different cases, but it always contains phosphate of lime.

(1401) All of these albuminoid substances are capable of existing both in a soluble and an insoluble form. In the animal fluids they occur in the soluble modification, whilst in the solid parts they frequently are found in the insoluble condition. The power of thus existing either in the solid or in the liquid state is of the greatest importance to the operations of animal life. It is necessary that these essential constituents of our frame should be able to exist in solution, in order that by the circulation of the blood they may be carried into every part of the body; and it is also necessary that they should be able to assume a solid form, to prevent the circulating fluids in their course from dissolving and washing away the delicate organs through which they pass.

These albuminous principles, either in their soluble or their insoluble condition, are readily dissolved by the aid of a gentle heat in a solution of potash or of soda: the addition of an acid to this liquid so obtained causes the separation of a greyish flocculent precipitate, termed by Mulder *protein*, while a slight odour of sulphuretted hydrogen is emitted, and a small quantity of phosphoric acid is also found in the solution. This precipitation is best effected by means of acetic acid, since the mineral acids are obstinately retained by the flocculi. When either of these principles, in its soluble form, is evaporated at a gentle heat, it yields a semitransparent friable mass, nearly insoluble in alcohol and ether. Indeed, the addition of alcohol to the aqueous solutions causes their coagulation. Their aqueous solutions are also precipitated by the addition of solutions of the salts of copper, of lead, and of mercury, as well as by infusion of galls.

Concentrated sulphuric acid dissolves the albuminoid substances with a brownish red colour, but the most characteristic tests for the proteic bodies are afforded by nitric and hydrochloric acids. Concentrated nitric acid produces in their solutions a coagulum of a bright orange colour, and gradually dissolves it with effervescence, or if they be in the insoluble condition, the tissue is stained yellow, and is slowly dissolved. Mulder considers this yellow substance to be a distinct compound, and names it *xanthoproteic acid*. Concentrated hydrochloric acid when gently warmed with albuminoid solutions produces a milk-white coagulum, which it dissolves slowly, forming a blue or violet-coloured liquid. It may farther be stated that acids generally produce coagulation of albuminoid substances when in solution, but that (with the exception of the metaphosphoric) when added in excess they redissolve the coagulum. On diluting these acid liquids with a moderate quantity of water, a precipitate occurs, but it disappears if the dilution be carried still farther. These acid solutions give a precipitate with the ferrocyanide and with the ferridcyanide of potassium, though the aqueous solution does not. Millon proposed to test for the protein-compounds by moistening the tissues supposed to contain them, with a solution of two parts of mercury in four of nitric acid, of sp. gr. 1·40. On the application of a temperature a little below that of boiling water, an intense red colour is developed, which is not destroyed by boiling with water, nor by exposure to the air. The gelatinous tissues, however, produce a similar coloration. This red colour is so intense that it may be perceived on adding the mercurial solution to a liquid containing not more than $\frac{1}{1000000}$th of its weight of albumen.

Both albumen and fibrin contain a small quantity (less than 2 per cent.) of sulphur and of phosphorus; casein likewise contains sulphur, but the phosphorus is absent. It is owing to the presence of sulphur that putrid eggs possess their peculiarly offensive odour. The sulphur is in the unoxidized condition, and this probably is also the case with the phosphorus. By the action of a solution of potash, both these elements are in great measure removed from the organic body, and when the alkaline liquid is neutralized with an acid, the protein is precipitated, whilst the phosphorus and most of the sulphur remain in the solution. The presence of unoxidized sulphur in the supernatant liquid may be shown by adding to the cold solution in potash, of one of these compounds (albumen for example), a few drops of a clear solution of oxide of lead in potash, formed by adding an excess of potash to a solution of acetate of lead. On applying heat to the solution, the albumen is decomposed, its sulphur is removed, whilst sulphide of potassium and hyposulphite of potash are produced; $4\ S + 3\ KO = 2\ KS + KO, S_2O_2$: the sulphide immediately shows itself by forming a brown precipitate of sulphide of lead, which renders the liquid dark-coloured and opaque; $PbO + KS = PbS + KO$. The phosphorus becomes oxidized and converted into phosphoric acid; it remains in the liquid, in which it may be discovered by the appropriate tests.

Many chemists, including Gerhardt among the number, regard all the substances of the albuminoid group as chemically identical, and as resulting from the combination of a single principle, which presents the characters of a feeble acid; the modifications in properties which it exhibits under the various forms of albumen, fibrin, and casein, being due to its combination with different bases, or saline bodies. This hypothesis, however, though probable, has not been actually proved to be true, and in the present state of science it is necessary to regard these bodies as distinct substances, which are convertible by vital processes one into the other, but each of which has its own peculiar functions in the organism.

The original view of Mulder was, that albumen, fibrin, and casein were derivatives of one fundamental azotised principle, which he termed *protein*; and that this substance by its union with different proportions of sulphur and of phosphorus, gave rise to the different modifications of the albuminoid group. Liebig has, however, shown that Mulder's protein always retains a small but variable amount of sulphur, and he denies the existence of protein as a separate body. It appears most likely that the substance termed protein by Mulder is merely the original body which was operated upon, but slightly modified in the course of the experiments, by the action of potash. The following table indicates the composition of 100 parts of protein according to the analysis of Mulder, and it gives a comparative view of the results of the analysis of albumen, fibrin, and casein, by the same chemist, from which it is apparent that the composition of these bodies is such that mere ultimate analyses are insufficient to distinguish between them. The analyses of legumin are discordant, and it appears doubtful whether Dumas and Cahours operated on a homogeneous substance (1408). In all cases the ashes have been deducted previous to calculating the composition in 100 parts :—

	Mulder.					Gobley.	Dumas and Cahours.	Bence Jones.
	Protein from Albumen.	Albumen from Hen's Eggs.	Fibrin.	Casein.	Globulin.	Vitellin from Hen's Eggs.	Legumin from Peas.	Legumin from Beans.
Carbon . .	53·7	53·5	52·7	53·83	54·5	52·26	50·53	55·05
Hydrogen .	7·0	7·0	6·9	7·15	6·9	7·25	6·91	7·59
Nitrogen .	14·2	15·5	15·4	15·65	16·5	15·06	18·15	15·89
Oxygen .	23·5	22·0	23·5	22·52	22·1	23·24	24·41	
Sulphur .	1·6	1·6	1·2	0·85		1·17		21·47
Phosphorus		0·4	0·3			1·02		
	100·0	100·0	100·0	100·0	100·0	100·00	100·00	100·00

The numerous experiments upon fibrin, albumen, and casein, made subsequently to these, by various chemists, completely confirm the accuracy of the results obtained by Mulder with these substances.

(1402) *Protein*? ($C_{36}H_{27}N_4O_{12} = C_{36}H_{25}N_4O_{10}, 2\ HO$?).—Mulder still maintains the existence of a substance free from sulphur, which he terms protein, and to which he assigns the formula above given. It has, however, never been procured free from sulphur. The gelatinous flocculi, obtained on neutralizing an alkaline solution of any albuminoid substance, if well washed and dried, furnish a yellowish, horny-looking, semi-transparent mass, which has, according to Mulder, the same composition, whether it be prepared from albumen, from fibrin, or from casein. Protein is destitute of taste and smell: it is insoluble in water, alcohol, and ether; but in water it swells up and becomes gelatinous in appearance. The alkalies dissolve it, and deposit it unaltered on neutralizing the solution with an acid. In the mineral acids it swells up and forms a jelly which retains a portion of acid; this acid jelly is insoluble in water, though an excess of the acid dissolves it, and deposits it unaltered on dilution. Diluted sulphuric acid if digested upon protein at 212° for some hours gradually decomposes it, and produces amongst other compounds a quantity of leucine.

When protein, or any compound which furnishes it, is boiled in water for several consecutive hours, the protein gradually combines with oxygen, and becomes converted into a soluble substance, termed by Mulder *teroxide of protein and ammonia*, ($H_4NO, 2C_{36}H_{25}N_4O_{13}, 3HO$?): this compound is insoluble in alcohol and in ether. Its aqueous solution is precipitated by the mineral acids, by solutions of chlorine, of tannic acid, and by the salts of lead, of silver, of zinc, and of iron; but not by ferrocyanide of potassium, or by salts of baryta. It forms neutral compounds with the alkalies; but if boiled with an excess of potash or of soda it emits ammonia. It is very probable that much of the material which figures in the analysis of animal products, as 'watery extractive animal matter' consists of this body; and if so, it forms an important substance in connexion with the metamorphosis of albumen and of fibrin into the products which are carried off by excretion from the system.

When a current of chlorine is transmitted through a dilute solution of albumen, a compound is separated in white flocculi, which Mulder regards as a definite compound of chlorous acid with protein. This substance when decomposed by ammonia, yields the ammoniacal teroxide of protein, just described. This same substance appears to exist in the *buffy coat* of the blood, which is formed upon the surface of the coagulum in blood drawn from patients suffering from certain acute inflammatory affections. In such cases, it is associated with an insoluble compound, originally described by Mulder as the *binoxide* of protein. The same chemist also regards this insoluble body as forming the principal constituent of the hair: it is of a yellowish colour, is soluble in alkalies, and is sparingly so in acetic acid. Mulder states that it is this compound which constitutes the insoluble residue obtained from fibrin after it has been boiled for many hours in water. It is probably similar to that found in horn; but the nature of this substance, and its relations to albumen, require further examination. Indeed, the existence of the whole of these protein compounds, as distinct principles, must be admitted to be very problematical.

(1403) Albumen.—The properties of this body when in solution are subject to considerable modification, according to the nature of the substances with which it is associated. The reactions of albumen from the white of the hen's egg (*ovalbumen*), therefore, differ in some respects from those afforded by albumen contained in the serum of blood (*seralbumen*), and this again from soluble albumen freed as far as possible from saline admixture; and all of these forms of albumen differ slightly from the albumen contained in the urine as secreted in Bright's disease.

Soluble albumen, in an aqueous solution, is a tasteless, somewhat glairy, colourless liquid, which exerts a left-handed rotatory action upon a ray of polarized light. A solution of albumen is readily coagulated by heat, and by the addition of various saline and acid liquids. It may be evaporated to dryness at a temperature not exceeding 120° F., and may be preserved in the form of a yellowish, brittle, transparent mass, which is insoluble in alcohol and in ether; but it may be slowly redissolved in lukewarm water; the solution being greatly promoted by the addition of a small quantity of chloride of sodium or of any other salt of the alkalies. A considerable portion of the albumen is, however, always left in the insoluble form. If white of egg, or serum, be evaporated to dryness *in vacuo*, then powdered and digested in a small quantity of cold water, the greater portion of the soluble salts are dissolved, and at the same time a considerable quantity of albumen is found in the liquid; the residue, after being thus freed from its soluble salts, is almost insoluble. Albumen, in its purest form, has a slightly acid reaction upon litmus.

The most remarkable peculiarity of albumen is its power of solidifying on the application of heat and of becoming insoluble. This coagulation begins at 140° F.; the solution, if concentrated, sets into a gelatinous mass, as is seen in the common process of boiling an egg hard; but when the liquid is very dilute, it simply becomes turbid. The albumen may, however, be separated by ebullition, provided that the solution be neutral or slightly acid; it then collects into flakes, which can be separated by filtration. Nothing is known of the cause of the coagulation of albumen by heat. When a solution of albumen containing alkali, such as serum or white of egg, is heated, a small quantity of sulphur is separated, and the liquid becomes rather more alkaline from the liberation of a portion of the soda from the coagulated mass.

Coagulated albumen, when dried, forms hard, horny, transparent masses, of a yellowish colour. When plunged into cold water it absorbs four or five times its bulk of this liquid, and becomes opaque and elastic. It is not soluble in water, but by long boiling in open vessels it undergoes gradual decomposition, and a soluble compound is obtained, which has the composition of teroxide of protein and ammonia (1402). If heated to 300° with a small quantity of water, in a sealed tube, the albumen is redissolved, and furnishes a liquid which does not coagulate by heat, but which when acidulated with acetic acid gives a precipitate with ferrocyanide of potassium.

Strong alcohol precipitates albumen from its aqueous solution; but if the alcohol be rendered slightly alkaline by the addition of potash, no coagulation ensues. Ether, if free from alcohol, does not occasion the coagulation of albumen, although it renders its concentrated solution viscid. Kreasote occasions its immediate coagulation. The concentrated mineral acids precipitate albumen in a coagulated form, but gradually decompose it and dissolve it, acting upon it as they do upon the compounds of protein generally: oil of vitriol dissolves it with a brownish red colour, nitric acid produces with it a lemon-yellow, and warm hydrochloric acid a violet-coloured solution after some hours' digestion. Nitric acid precipitates it, and when dilute, does not redissolve the precipitate. Hydrochloric acid precipitates it and redissolves the coagulum; the solution when poured into a small quantity of water becomes milky, but is rendered clear by the further addition of water. Dilute sulphuric acid produces no precipitate till the liquid is boiled: the clear solution in concentrated sulphuric acid is not precipitated when diluted with water. Metaphosphoric acid causes an immediate coagulation of albumen; but the other varieties of phosphoric acid produce no such effect. Acetic acid, and the organic acids generally, except the modification of tannic acid which is contained in infusion of galls, do not produce any precipitate in solutions of albumen.

The solutions of albumen in the organic acids are not coagulated by boiling, but a pellicle gradually forms over the surface during evaporation; the addition of a saline solution, such as sulphate of soda or chloride of sodium, causes the albumen to separate from these solutions. The precipitates thus obtained are generally soluble in pure water; *precipitated* albumen is, therefore, not necessarily in the *coagulated* form. If a solution of white of egg be rendered accurately neutral by the addition of acetic acid, and then be diluted, flocculi of albumen are precipitated, but they are redissolved when treated with a solution of common salt or of nitre.

Solutions of alum, and of many of the metallic salts, such as those of copper, of lead, of mercury, and of silver, precipitate solutions of albumen. It is, therefore, useful to administer whites of eggs in the liquid form in cases where poisoning from swallowing any of the salts of these metals is suspected to have occurred; the remedy is a safe one, and it can do no harm; whilst if the poison have really been taken, the albumen decomposes the salt, and generally enters into combination both with the acid and the base; the albumen sheathing the stomach from the influence of the poison, whilst other measures are in preparation for effecting its removal from the system.

Effect of Bases on Albumen.—The presence of an alkali in liquids containing albumen considerably modifies the reactions; if the alkali be present in large quantity, the solution does not coagulate when heated, but a pellicle forms over the surface during the evaporation, thus exhibiting an appearance similar to that observed when milk and other solutions of casein are exposed to the air whilst hot.

Albumen forms definite compounds with the alkalies and other metallic oxides. Coagulated albumen is dissolved freely by solution of the alkalies, and in certain proportions it even neutralizes their action upon test paper. If a concentrated solution of albumen be mixed with one of potash, a gelatinous mass of *albuminate of potash* is formed, from which, by washing with cold water, the excess of alkali may be removed; it retains 5·4 per cent. of potash (Lieberkuhn). If the gelatinous mass be washed with alcohol and then with water, it is insoluble in boiling water and also in boiling alcohol; but if it be washed with cold water only, the residue is soluble both in boiling water and in boiling alcohol. The aqueous solution of albuminate of potash is not coagulated by boiling it, but on the addition of a small quantity of acetic, tartaric, or phosphoric acid, a white coagulum is produced, which is readily dissolved by an excess of acid. These characters resemble those of casein, and some chemists have supposed that casein is simply an albuminate of potash. The coagulum obtained by the addition of acetic acid to the solution of albuminate of potash, when well washed, furnishes nearly pure albumen. It leaves scarcely any ash on incineration.

The albuminate of *soda* resembles that of potash, and may be formed in a similar manner. The animal fluids in which albumen occurs, such as the white of the egg and the serum of the blood, are very slightly alkaline, the proportion of alkali not exceeding 1·58 per cent. in ovalbumen (Lehmann). Even this small proportion renders the albumen more soluble, and prevents its complete coagulation on boiling, a portion of albumen remaining dissolved and forming what is often termed *albuminate* of soda: and that portion of the albumen which does coagulate does not collect into flocculi. The albuminate of soda may be readily decomposed by neutralizing it with acetic acid; on afterwards boiling it, the albumen separates in coherent flocks. It is also to be remarked that the albumen may be made to separate from the slightly alkaline liquid by boiling it after the addition of a neutral salt, such as sulphate of soda, common salt, or muriate of ammonia. These are points which require attention in the analysis of animal liquids, in which the quantitative separation of albumen is necessary. Gerhardt is disposed to view serum and the white of eggs as containing a definite bialbuminate of soda, and adopting Lieberkuhn's formula for albumen it would be $(HO, NaO, C_{144}H_{110}N_{18}S_2O_{42}, 2\ Aq)$. Such formulæ, however, can only be regarded as approximations.

According to Lieberkuhn, the compound of albumen with *oxide of silver* is (AgO, HO, $C_{144}H_{110}N_{18}S_2O_{42}$, 2 Aq); that of *copper* (2 CuO, $C_{144}H_{110}N_{18}S_2O_{42}$, 2 Aq); the latter substance is soluble in an excess of solution of sulphate of copper. The compound of albumen with oxide of *lead* is obtained by adding subacetate of lead to a solution of albumen; it is readily decomposed by all the acids. The albuminate of *mercury* is formed when a solution of white of egg is mixed with one of corrosive sublimate: it is very insoluble in pure water, but it is dissolved by a solution of common salt.

Preparation.—The preparation of pure albumen in the *coagulated form* may be effected by precipitating white of egg by means of hydrochloric acid, washing with the same acid in a diluted form, and then dissolving in water: this solution is precipitated by carbonate of ammonia; the coagulum is washed, dried, and subsequently powdered, after which it is digested in alcohol and in ether, in order to remove traces of adhering fatty matters. It may also be obtained by decomposing albuminate of potash by means of acetic acid.

In the *soluble form* it is doubtful whether it be possible to free the albumen perfectly from salts. One method by which this object is nearly attained consists in neutralizing dilute white of egg with acetic acid; the liquid is then evaporated to dryness in a platinum capsule at a temperature below 120°, after which the powdered residue is digested in very weak alcohol.

Wurtz considers that a pure soluble albumen may be obtained in the following manner: white of egg is well agitated with twice its volume of water and strained through linen in order to remove the membranous flocculi: the filtered portion is then mixed with a solution of subacetate of lead, in quantity insufficient to throw down the whole of the albumen. The copious precipitate thus obtained must be well washed, suspended in water, and decomposed by means of a current of carbonic acid gas, when the lead is separated in the form of carbonate, and the liberated albumen becomes dissolved. The solution is filtered through paper freed from saline matter by washing with a weak acid. It however retains traces of lead, which may be removed by transmitting sulphuretted hydrogen and heating the liquid to 140°, when the first flocculi of coagulated albumen which are thus formed carry with them the whole of the sulphide of lead, and may be removed by filtration. The liquid is finally evaporated at a temperature below 120°.

No method is known by which the absolute purity of albumen can be ascertained. Its combining equivalent is also uncertain, since it forms no definite compound upon the purity of which a decided opinion can be formed.

Sources of Albumen.—Albumen is a very abundant constituent of the animal body: it constitutes about 7 per cent. of the entire mass of the blood; it is an essential component both of lymph and of chyle; and it is abundant in all serous exudations, although it is found in these fluids in smaller proportion than in the serum of the blood. It is also contained in large proportion in many of the soft solids of the body, as for example, in the brain, the kidneys, the liver, and the pancreas, in all of which it exists in the uncoagulated form. The liquid of the pancreas appears to be the only secretion in which it occurs in health. It is never found in the excreta except under the influence of disease: thus it is occasionally poured out from the mucous membrane of the bowels in cases of intestinal catarrh, and has been repeatedly found in the alvine dejections in cases of dysentery, as well as in those of Asiatic cholera. It is likewise often met with in the urine in acute febrile affections, as well as in some chronic affections of the heart, liver, and kidneys, especially in the disease known as *morbus Brightii*. Its occurrence in the ovum is general, and is familiarly illustrated in the case of the eggs of birds.

The juice of many plants, such as that of carrots, turnips, and cabbages, when heated, becomes turbid, from the coagulation of a substance which analysis shows to have the same composition as albumen, and with which it coincides in all important particulars. Wheat flour likewise contains an azotised substance which is soluble in cold water, forming a solution which yields greyish flocculi of albumen on evaporation.

Paralbumen is the name given by Scherer to a substance obtained from the liquid of ovarian dropsy. Its solution is precipitated by alcohol, but the flocculi are redissolved by water at 100°, and it is only imperfectly coagulated by heat. Many other varieties of albumen which have been described probably arise from the modifying effects of salts upon albumen.

(1404) *Globulin*, or *Crystallin*, is a substance which closely resembles albumen. It occurs mixed with albumen in the cells of the crystalline lens in a very concentrated solution, forming, according to Simon, from 10 to 14 per cent. of the dry lens.*

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* Lehmann, in his experiments upon this substance, appears not to have separated the albumen, and hence the description which he gives of it differs from that of Simon, who removed this impurity.

typhus, chlorosis, &c., it is frequently, but not uniformly, slightly diminished, though by long fasting it is somewhat increased in quantity. Lymph does not usually contain more than 0·4 or 0·5 parts per 1000. In the chyle of animals it has been found to vary from 0·7 to 7·0 per 1000.

Fibrin, in the form of muscular tissue, constitutes a large proportion of the soft parts of animals. It occurs in muscle arranged in bundles of fibres, and from this circumstance the name of fibrin derives its origin. Muscular fibrin, however, presents several points of difference from the fibrin obtained from the blood. According to Liebig, fibrin may also be obtained from the juice of plants, and it exists in the gluten of wheat.

Preparation.—*Blood-fibrin* may be obtained in a state of tolerable purity by whipping up freshly drawn blood with a bundle of twigs: in the act of coagulation the fibrin attaches itself in soft, white, opaque, elastic strings to the twigs, and may be afterwards washed clean by maceration and kneading in water till it is free from colour. When dry, fibrin forms a horny, yellowish, or grey solid.

The reactions of fibrin in the solid form are similar to those of coagulated albumen, except that fibrin decomposes deutoxide of hydrogen with effervescence, whilst albumen produces no such effect; but fibrin by long boiling in water is also rendered equally inert. When fibrin is heated to 300° with a small quantity of water, in a sealed tube, it is redissolved, and forms a solution which becomes coagulated by acids, and resembles that formed by albumen under similar circumstances. The coagulation of fibrin is prevented by allowing the blood, at the moment of its efflux from the body, to mix with solutions of certain salts, such as carbonate, or nitrate of potash, acetate, or sulphate of soda, and chloride of sodium. The fibrin of venous blood, before exposure to the oxygen of the air, is freely soluble in a solution containing about one-sixth of its weight of nitre, as well as in similar solutions of the alkaline sulphates, acetates, phosphates, and chlorides. This solution becomes coagulated like albumen when heated, but is precipitated by acetic acid; when exposed to the air, the solution absorbs oxygen and deposits insoluble flocculi. Fibrin is freely soluble in dilute solutions of potash or of soda, and the alkaline liquid presents many of the characters of albuminate of soda, and on neutralizing the solution with acetic or phosphoric acid, the fibrin is re-precipitated: if the alkaline solution be mixed with metallic salts it yields precipitates similar to those formed with albumen. The solutions, both of fibrin and of albumen, in acetic acid, are precipitated on the addition of ferrocyanide of potassium, a character by which they are at once distinguished from gelatin, which gives no precipitate under similar circumstances. If the acetic solution of fibrin be neutralized by potash, it is precipitated by the same reagents as albumen, but it does not become coagulated when heated. There is a marked difference between the action of oxygen upon albumen and fibrin. Scherer found that when freshly drawn serum, or white of egg, was exposed to the action of oxygen gas, confined over mercury, scarcely any absorption of the gas occurs, and little or no carbonic acid is evolved; coagulated fibrin, on the other hand, when exposed in a moist state to the air, gradually absorbs oxygen, and emits carbonic acid, and in a few days becomes putrid. By long boiling in water it is gradually dissolved, and becomes oxidized. Albumen is similarly altered. Analysis appears to prove that fibrin is a body which is more highly oxidized than albumen (see Table, p. 651); and coagulated fibrin, as it exists in muscle, is also more fully oxidized than that which separates from the blood on standing. Lehmann's view, that blood-fibrin is a stage of transition between albuminous matter and the animal tissues, is thus rendered highly probable. It appears also, from the analyses of Dumas and others, to contain about 1 per cent. more of nitrogen than albumen.

(1406) *Varieties of Fibrin.*—The observations of Liebig on the different forms of fibrin are interesting. He finds that moist *blood-fibrin*, if left under water in a warm place in a vessel loosely covered, putrefies, and gradually becomes dissolved; in one of his experiments, after the fibrin had been macerating for a fortnight, a liquid was obtained, which coagulated when heated, and presented many of the characters of a solution of albumen. The solution likewise contained leucine, and acetic and valeric acid, besides some other acid substances, which have been but incompletely examined. Hydrosulphate of ammonia is also formed. If the water in which the fibrin is digested be previously mixed with one-tenth of its bulk of hydrochloric acid, blood fibrin swells up slowly into a gelatinous mass, which, on the addition of a stronger acid, shrinks to nearly its original volume, and again swells up when put into water, but it does not form a true solution.

The *fibrin of muscle*, on the contrary, after it has been well washed and pressed, to free it from soluble matters, is dissolved more or less completely by dilute hydrochloric acid. If the acid contained in this solution be neutralized by an alkali, a coagulum occurs, which is readily dissolved by an excess of alkali, or even this latter solution becomes coagulated, on boiling, like white of egg. On the addition of ammonia to the solution of fibrin in hydrochloric acid, the muscle fibrin is precipitated, and may be purified by successive washings in water, alcohol, and ether. The muscle of different animals varies in solubility; that of the fowl, and of beef, was found to be almost wholly soluble, that of mutton was less so, whilst in the muscular fibrin of veal the insoluble portion amounted to nearly one-half—this residue contained the fat and the vascular portions, besides a quantity of fibrin which resembled blood-fibrin in characters. The soluble portion was found to contain less nitrogen than the blood-fibrin. When fibrin is treated with acetic acid, and viewed by the microscope, it is found to consist of two portions, one of which is granular, and soluble in acetic acid, while the other is fibrous and insoluble. The proportion of these two components differs widely in different specimens. The ultimate composition of these two constituents appears to be very nearly the same.

The portion of the gluten of wheat flour which is insoluble in hot alcohol, and in ether, is regarded by Liebig and by Dumas as coagulated fibrin. It is soluble in very dilute hydrochloric acid, like the fibrin of muscle.

(1407) CASEIN is found abundantly in milk, of which it constitutes nearly 3 per cent. Its solutions do not become coagulated by boiling; they, however, present a reaction nearly as characteristic: the hot liquid gradually absorbs oxygen, and in consequence, a pellicle, which is insoluble in water, is gradually formed upon the surface.

Preparation.—Casein, in the *soluble* form, as present in milk, appears to owe its solubility to the presence of a certain proportion of free alkali. It cannot be obtained free from salts. If skimmed milk be evaporated to dryness at a gentle heat, and then digested with ether to remove the fat, on treating the residue with water, the lactose and a portion of the casein are redissolved, and, on the addition of alcohol, a considerable portion of the lactose is separated. The alcoholic liquid contains casein, still contaminated with lactose and with salts.

Casein may be obtained in the *coagulated* form nearly pure by the following process:—Skimmed milk is to be curdled with dilute sulphuric acid. The curd, after being well washed with water, is to be dissolved in carbonate of soda, and suffered to stand undisturbed for twenty-four hours or more, to allow the oil to rise to the surface; this is to be skimmed off, and the casein again precipitated by an acid, and well washed; after repeating this operation a second time, the coagulum is to be digested in alcohol and ether, and again dried; but it cannot be perfectly freed from the saline matters, which adhere to it with great tenacity.

Casein may also be obtained by coagulating skimmed milk by means of hydrochloric acid, and washing the curd first with water, then with water acidulated with 2 or 3 per cent. of hydrochloric acid, and finally with pure water; a glutinous mass is thus obtained, which is slowly dissolved by digestion at 110° in a large quantity of water. The solution, after being filtered, is precipitated by the cautious addition of carbonate of ammonia, the coagulum is washed with water, and then digested successively with alcohol and ether.

Properties.—Casein in solution is immediately coagulated by acids. An excess of acetic or of oxalic acid dissolves the coagulum, but it is re-precipitated from its acetic solution on the addition of one of the mineral acids. According to Bouchardat, water, containing 1-2000th of its weight of hydrochloric acid, forms with casein a colourless solution, which produces left-handed rotation of a ray of polarized light. If these acid solutions be evaporated at a high temperature, a pellicle of insoluble casein is formed over their surface. Mulder considers that when the mineral acids are employed to coagulate casein, they form definite compounds with it, the acid may, however, be entirely removed by washing. With strong nitric, sulphuric, and hydrochloric acids, casein produces the same reactions as albumen; and its acetic solution gives a similar precipitate with ferrocyanide of potassium. Soluble casein is sparingly soluble in cold alcohol, but more freely so in hot alcohol. The stronger acids produce no precipitate in this alcoholic solution, which, however, is immediately coagulated by infusion of galls. The solubility of casein in water is not destroyed by the action of alcohol, for the residue obtained on evaporating both the aqueous and the alcoholic solutions to dryness may be redissolved in water.

Action of Bases and of Salts.—Coagulated casein is readily dissolved by solutions of the alkalies, and of the alkaline carbonates; and if the solution be very feebly alkaline, the alkaline reaction may be completely neutralized by the casein. Solutions of common salt, of nitrate of potash, and of muriate of ammonia, likewise dissolve casein with facility, and these solutions, when evaporated by the aid of heat, become covered with an insoluble pellicle. Casein also unites with the alkaline earths and forms compounds which are insoluble in water. If a piece of poor cheese, which consists principally of casein, be reduced to a paste with water, and mixed with slaked lime, it produces a tenacious lute, which sets very hard, and may be used for cementing pieces of broken earthenware. In consequence of the tendency to the formation of these insoluble compounds, a solution of casein is precipitated by salts of lime or by sulphate of magnesia, upon the application of heat to the mixture: this reaction is very characteristic of casein. Most of the metallic salts, such, for instance, as acetate and subacetate of lead, sulphate of copper, subnitrate of mercury, and corrosive sublimate, occasion precipitates in the cold with solutions of casein.

But the most important and remarkable form under which the coagulation of casein occurs, is that which is produced by the secretion from the mucous membrane of the stomach. Advantage is taken of this in the manufacture of cheese, which consists essentially of the coagulated casein of milk. The coagulation is effected by means of the substance called *rennet,* which consists of the inner membrane of the fourth stomach of the calf, after it has been salted and dried. When milk is maintained for a few hours at a gentle heat in contact with rennet (or with an infusion of rennet prepared at a low temperature), the casein becomes entirely coagulated, carrying with it the fatty matters which were held in suspension by the milk, and leaving a clear straw-coloured liquid known as *whey.* It was at one time supposed that the rennet acted by converting the sugar of milk into lactic acid, and that the lactic acid was the real agent in effecting the coagulation, but this view is no longer tenable, for it appears that this coagulation occurs equally well with milk which has been purposely rendered slightly alkaline (Selmi, Heintz), and with an aqueous solution of casein; the action of rennet is therefore as yet unexplained. The coagulum, or *curd* thus obtained, when submitted to strong pressure, forms cheese. This curd is dissolved with difficulty by alkaline solutions. New cheese has but little flavour; when kept for some time the fatty and nitrogenous substances undergo partial decomposition, and liberate ammonia, valeric and butyric acids, and other compounds which impart pungency to old cheese.

Casein has not been detected with certainty anywhere but in the milk of animals, which contains it in very variable quantity, the amount depending greatly upon the period of lactation at which the milk is examined. Its amount also varies greatly in the milk of different species of animals. In the human female it has been found to constitute from 31 to 35 parts in 1000; in that of the cow, from 30 to 41; in that of the dog, from 80 to 146, and in that of the ass, from 19 to 23 parts in 1000.

(1408) *Legumin.*—The seeds of most leguminous plants, as well as the sweet and the bitter almond, contain a substance which presents a close analogy in properties with the casein of milk. Liebig indeed considers it to be identical with this substance, but the analyses of Dumas and Cahours indicate a difference in composition between the two bodies. There is however some doubt whether the chemists last named operated upon a homogeneous substance.

Legumin is usually extracted from peas or from almonds, by digesting the pulp of the crushed seeds in warm water for two or three hours. The undissolved portion is strained off by means of linen, and the turbid liquid is allowed to deposit the starch which it holds in suspension: it is then filtered and mixed with dilute acetic acid. A white flocculent precipitate is thus formed, which must be collected on a filter and washed. It is then dried, powdered, and digested, first in alcohol and afterwards in ether. In this form it was analysed by Dumas and Cahours. Rochleder however considers that it is not perfectly pure, since this substance is not entirely soluble in a cold concentrated solution of potash, which leaves a flocculent matter. The alkaline solution may be decanted from the undissolved flocculi, and again precipitated by the addition of acetic acid. The legumin thus obtained is regarded by Rochleder as pure.

According to Dumas and Cahours, legumin is precipitated from its concentrated solutions in pearly flocculi by the addition of acetic acid. It is redissolved by acetic acid in excess, and by many other vegetable acids; it is also soluble in ammonia and in dilute solutions of the alkalies. It is insoluble in boiling water, and in cold alcohol and ether. Cold water dissolves it in considerable quantity, and the liquid, when heated to ebullition, deposits it in flocculi resembling those of coagulated albumen. The aqueous solution of legumin obtained by digesting peas in water is not coagulated by heat, according to Liebig, but on evaporation it forms insoluble pellicles resembling those yielded by solutions of casein Legumin is associated in the seed with considerable quantities of the phosphates of potash, of lime, and of magnesia. It is coagulated by rennet like the casein of milk, and the Chinese make a kind of cheese from peas and beans. Dried peas contain about one-fourth of their weight of legumin.

§ II. GELATIGENOUS SUBSTANCES.

(1409) The substances contained in the second group of azotised bodies have hitherto been found only in animals. They contain a smaller amount of carbon and a larger quantity of nitrogen than those of the protein group. The proportion of sulphur is also considerably less. The gelatigenous bodies consist of two principal varieties; viz., those which yield *gelatin*, and those which yield *chondrin:* neither gelatin nor chondrin appears to exist in the soluble form in the animal body, but it is in all cases the result of the prolonged action of boiling water upon the gelatigenous or chondrin-producing tissues.

According to the researches of Mulder, of Scherer, of Fremy, and of other chemists, the composition of gelatin is identical with that of the tissue which yields it by boiling. Chevreul found that a given quantity of tendinous matter when converted into gelatin by boiling it with water was not altered in weight. The following table exhibits the composition of gelatin, chondrin, and some gelatigenous tissues:—

	Fremy.	Scherer.	Mulder.		Scherer.
	Ossein.	Sclerotica.	Gelatin.	Chondrin.	Cartilage.
Carbon . .	50·4	50·1	50·40	49·97	50·5
Hydrogen	6·5	7·1	6·64	6·63	7·0
Nitrogen .	16·9	18·7	18·34	14·44	14·9
Sulphur .	26·2	24·1	24·62	0·38	27·6
Oxygen .				28·58	
	100·0	100·0	100·00	100·00	100·0

The quantity of nitrogen given in Fremy's analysis of ossein is probably too low, for the same chemist found in it upon another occasion as much as 17·86 per cent. of nitrogen. Schlieper has shown that gelatin and the gelatigenous tissues contain a small quantity of sulphur, amounting in isinglass to 0·6 per cent. It will be observed that the composition of chondrin differs from that of gelatin in containing more oxygen and less nitrogen; whilst the percentage of carbon and of hydrogen is the same in both substances.

(1410) GELATIN is an azotised principle which hitherto has been obtained from animal substances only. Certain structures (the principal of which are the white fibrous tissue, the cellular tissue, the skin, the serous membranes, and the organic constituent of bone), when boiled with water, yield a compound, which if the solution contain more than 1 per cent. of it, causes the liquid to gelatinize on cooling, hence its name of *gelatin;* this substance does not appear to exist in a free state, but is developed by the action of boiling water upon the tissues above mentioned: its solution, when evaporated to dryness, leaves a brownish-yellow transparent mass. *Isinglass* which is prepared from the inner membrane of the floating bladder of sturgeons and other fishes, when boiled with water, furnishes gelatin in a state of considerable purity. *Glue* is a variety of gelatin of inferior quality. *Size*, as prepared from parchment, is another form of gelatin which is met with in commerce.

Gelatin softens and swells up in cold water, but is not dissolved until the liquid is warmed: it is insoluble in alcohol and in ether. It may be precipitated from its aqueous solution by the addition of an excess of alcohol, when it falls in white flocculi, which are nearly free from saline compounds. Its solution is without taste or smell: it is abundantly precipitated by solutions of corrosive sublimate, and of bichloride of platinum, as well as by the infusion of galls. The compound which gelatin forms with tannic acid is the basis of leather; it is of a buff colour, and is formed even in very dilute solutions. Albumen is also precipitated by the same solutions, but gelatin may be distinguished from albumen, since it is not rendered turbid as albumen is, by the addition of ferrocyanide of potassium to its solution in acetic acid. Salts of alumina, of lead, of copper, and of iron, do not produce any precipitates in a solution of gelatin, but if a solution of potash be added to the mixture of gelatin with alum, or with persulphate of iron, the subsulphate of alumina or of iron which is formed carries down a large proportion of gelatin. In a dissolved condition gelatin soon becomes acid on exposure to air, and then loses its gelatinous character. Gelatin is capable of dissolving a considerable quantity of phosphate of lime. By the frequent boiling of its aqueous solution, gelatin is converted into an isomeric compound which does not possess the faculty of gelatinizing as the liquid cools. Chlorine precipitates gelatin completely, forming with it a peculiar white elastic compound which appears to consist of gelatin in combination with hypochlorous acid; this compound when treated with ammonia, yields nitrogen, muriate of ammonia, and unchanged gelatin. Solutions of gelatin are not rendered turbid by the addition of acids. Concentrated sulphuric acid dissolves gelatin without change of colour, and gradually converts it into glycocine, leucine, and some other bodies. Gerhardt found that when isinglass was boiled for some days with dilute sulphuric acid, sulphate of ammonia was formed, and a considerable quantity of a saccharine body which was susceptible of the alcoholic fermentation. Nitric acid produces oxalic acid amongst other substances.

A solution of gelatin to which the alkalies have been added in small quantity loses its faculty of gelatinizing, but the liquid on being neutralized gives no protein. Gelatin is decomposed by strong alkaline solutions; at a boiling temperature ammonia is evolved, and leucine and glycocine are amongst the products.

CHONDRIN differs from gelatin in composition: it is also coagulated by the vegetable acids, such as acetic acid, as well as by alum, and by the neutral and the basic acetates of lead, none of which yield precipitates with gelatin. Most of these precipitates are soluble in an excess of the precipitant.

Chondrin is obtained by boiling the cornea of the eye, or any of the permanent cartilages, with water for some hours; it may also be obtained from the primary cartilages prior to ossification. Its solution gelatinizes on cooling. It is remarkable that when a permanent cartilage becomes ossified, it yields not chondrin but gelatin by boiling with water.

Preparation of Glue and Size.

(1411) The preparation of gelatin on a large scale gives rise to a branch of industry of considerable importance, viz., the manufacture of glue and size.

The strongest glue is obtained from the parings of ox-hides, and from the ears and refuse trimmings of thick hides in general, which yield from 45 to 50 per cent. of glue. These clippings are first steeped for some days in lime water, to remove the hair, the blood, and other impurities; they are then washed in cold water, and are placed to drain upon a sloping pavement, in layers of two or three inches thick, and are turned over once or twice a day: the quicklime thus absorbs carbonic acid from the air, and becomes converted into chalk; so that the injurious effects of lime at a boiling heat upon the gelatin are prevented. The washed clippings are next introduced into a copper furnished with a perforated false bottom which is filled to two-thirds of its capacity with rain water; frequently the animal matters are put first of all into a coarse rope cloth, and the whole is placed in the cauldron, a precaution which prevents the portions of skin when they begin to gelatinize from adhering to the bottom and sides of the boiler, and so becoming burned; fresh portions of clippings are added as the animal matters gradually sink down into the liquid which is kept gently boiling. A still better method consists in boiling the liquid by the injection of steam under moderate pressure, by which means the direct application of fire to the boiler is avoided. As soon as a portion of the liquid sets into a firm jelly on cooling, the fire is checked, and the solution is allowed to run into a deep vessel or *settling back*, where it is kept warm for some hours to allow the impurities to subside. The undissolved matters contained in the cloth are again boiled with water, and yield an inferior description of glue; if boiled a third time they give a still weaker gelatinous product or size: the refuse, after this treatment, may still be advantageously applied as manure.

From the settling back, the solution is transferred to long wooden boxes or coolers, in which it gelatinizes; when sufficiently solid it is removed, cut into blocks, and each block is split by a wire frame into slices. The slices of moist glue are then laid upon nets placed in a wooden frame, and are so arranged in lofts as to allow free circulation of air. These cakes of glue are turned over two or three times daily, and the marks which are seen upon the glue exposed for sale, are those left by the threads of the nets. This operation of drying is the most delicate part of the manufacture, since at this stage much of the success of the operation depends upon the state of the weather. A sudden rise of temperature might liquefy the whole; the occurrence of a fog might render it mouldy, or a frost might split all the cakes into fragments. Spring and autumn are found to be the most favourable seasons for the manufacture of glue. After the drying has proceeded to a certain extent in the open air, the process may advantageously be shortened by the use of artificial heat from a stove.

When glue is properly made, it should be of a pale brown colour, hard, brittle, and should break with a smooth, glassy fracture. Cold water does not dissolve glue, but merely softens it, and causes it to swell up.

Size is a less tenacious kind of glue, and is chiefly made from parings of parchment, and of the thinner kinds of skins. It is almost entirely used in the gelatinous condition, so that the precarious process of drying is dispensed with. Much of the gelatin at present sold in fine shreds for use in confectionary is obtained from clippings of hides, which are boiled with water till they form a very liquid size, which is allowed to become clear by standing, and is then dried in very thin sheets, and afterwards cut up into shreds.

Preparation of Leather.

(1412) The hides of animals, like the soft parts in general, are prone to putrefaction and decomposition, if kept in a flexible and moist condition, and when allowed to dry, they become too rigid and brittle to allow of their employment for a number of purposes, to which they would otherwise be admirably adapted.

The operations of the tanner have in view the preservation of the hide from decay, and the preparation of a material possessed of the requisite suppleness, tenacity, and power of resisting the action of moisture.

The hides of different animals vary very much in thickness. The hippopotamus is furnished with a hide which is in some parts between one and two inches in thickness, whilst the leather produced from the skins of the lamb and of the kid does not equal ordinary pasteboard in thickness.

The thicker kinds of leather receive the general name of *hides;* and the strongest part of these hides which cover the back of the animal, constitute the *butts.* Ox-hides, the most valuable of which are those imported from the plains of South America, and from the Cape of Good Hope, yield the principal portion of this leather, which is largely consumed for the soles of boots and shoes; for harness, and for articles requiring much strength and durability. The upper leathers of boots and shoes are chiefly made of calves' and seals' skins; whilst for book-binding, for aprons, and for ordinary dyed leathers, the leather furnished by sheep skins constitutes the material principally used.

The skin of most animals is highly elastic; it consists of two portions which are quite distinct in chemical composition; an outer thin superficial layer, the *epidermis,* which dips down and lines the tubes containing the roots of the hair, and which rises in blisters after a scald. This is composed of a pellicle which resembles horny matter in composition; it is stained yellow permanently by the action of concentrated nitric acid: beneath this is the cellular layer, termed the *rete mucosum,* in which the colouring matter resides, but which is now generally regarded as a less compact portion of the epidermis: and below this is the thick sensitive vascular integument or *dermis,* which constitutes the true skin. When the dermis is boiled with water for some hours, it becomes dissolved, leaving the vascular parts, which can be removed by straining through linen or flannel; the clear liquid is nearly colourless; it gelatinizes on cooling, and consists mainly of gelatin. It gives with tincture of galls the well-known insoluble precipitate, by which such solutions are characterized.

Excepting in those cases where it is desired to preserve the hair, as in the different species of furs, the preliminary steps in the preparation of all skins are pretty much the same, whatever the use to which the leather is applied, but greater care is requisite *the beam*, and upon this, with a two-handled knife, the hide is scraped on the hair side to remove the epidermis and hair. By this operation the upper surface of the cuticle marked by the insertions of the hair is exposed; it is of a denser structure than the layers of cuticle below, and it forms what is called the *grain* of the skin; great care is taken not to injure this grain, as such injury impairs the quality of the leather, and much reduces its value. The hair having been removed, the hide is once more rinsed and scraped upon the beam, on the flesh side, to remove any irregularities, and adhering loose cellular tissue.

The cleansed hide is then immersed for twelve hours in a bath of weak sulphuric acid and water (1 part of acid and 1000 of water), which '*raises*' the skin, that is to say, makes it swell, opens its pores, removes adhering lime, and fits it for the actual operation of tanning. Care must be taken to avoid an excess of sulphuric acid, as it is liable to injure the texture of the hide. The removal of lime from the skin is a process of great importance, since, owing to the circumstance of the astringent matter being of an acid character, it would combine with the lime, instead of with the gelatin, and would form a harsh, insoluble compound within the pores of the skin, which would impair the suppleness of the leather.

(1413) 1. *Tanning.*—Up to this point the preparation of the skin is very similar for each kind of leather; when the process of tanning is to be performed, it is conducted in the manner now to be described.

The process of tanning is a very slow one. A weak infusion of bark, called *ooze*, is first prepared and pumped off into rectangular pits, six or eight feet deep, sunk in the earth, and lined with wooden planking; into these the hides are introduced, one by one, in an extended state. These pits of weak ooze are termed *handlers*, from the circumstance that the hides are for some weeks daily transferred from one pit to another, into oozes of gradually increasing strength: in about six weeks they are ready for the pits termed *layers*. In these pits the partially tanned hides are placed, each hide being separated from the one above and the one below it by a layer of coarsely ground oak bark; the pits are then filled up with water. Here the hides remain for about three months, and are then transferred to another pit, and similarly treated; but the hides which before were uppermost, and consequently in the weakest part of the infusion, now are undermost, and in the strongest part. Sometimes the hides require to be passed a third and placed nearly vertically, the object of this operation being to equalize the thickness of the skin in its different parts. It is then thrown into water and worked while moist upon a flat stone table with the flesh-side downwards. It is thus uniformly thinned out and stretched. Here it is next *stuffed* or *dubbed*, that is to say, it is thoroughly impregnated with a mixture of coarse fish oil and tallow, after which it is hung up in a loft to dry and allow the oil completely to penetrate the leather and take the place of the water.

When dry, the skin is rendered supple and 'grained' by rubbing it first on the flesh side, after folding the grain side inwards, with a grooved ball of box-wood; the operation is then repeated on the grain side. In this state, after another scraping on the flesh side or *whitening* it is ready to be stored away. Previous to sale, however, another process, technically termed *waxing*, is performed. This consists merely in rubbing in upon the flesh side, a mixture of lampblack and oil, with a hard brush. A coat of tallow and size is then rubbed over this with a sponge; it is polished with a ball of glass, and a final coat of thin size completes the operations of the currier. For ladies' shoes the skin is blackened on the grain side, which is easily effected by rubbing it over with a solution of sulphate of iron; the astringent matter of the leather immediately strikes a deep inky black with the copperas; a weak alkaline liquid is brushed over the whole, the skin is allowed to dry, it is then grained, and finished off with a coat of oil and tallow.

(1414) 2. *Morocco Leather.*—The thin kinds of leather which are dyed and used for ornamental purposes, as for coach linings, chair-covers, book-binding, &c., are tanned differently, but much more expeditiously than hides. The finest kind of this leather is made from the skin of the Barbary goat, and hence the term *Morocco leather* as commonly applied to it. In the preparation of these skins the wool or hair is removed in the usual way, and the lime is then worked out by a process termed *abating*. In this operation the skins are put into a weak solution of an ammoniacal salt (dog's dung being the material preferred); the lime forms a soluble compound with the acid of the salt, setting ammonia at liberty; this softens the skin, and at length renders it so porous that when a portion of air is included in a fold of the skin the air may be squeezed through it. The skin is next cleansed on the beam, and is sewed up in the form of a bag, the grain side outwards, and is ready for the *sumaching* or tanning, which is accomplished in about twenty-four hours. A weak and warm infusion of sumach is prepared in a large tub, a portion of sumach leaves and of a stronger infusion is poured into the bag formed by sewing up the skin, and this, when distended with air, is tied up and thrown into the vat, where the floating bags are kept in constant motion for some hours, after which they are piled up on a sloping shelf on the side of the vat, where, by mutual pressure, a portion of the tanning solution is forced through the pores of the skin. The operation is repeated with a stronger infusion of sumach; after which the skins are cut open, washed, dried, and subsequently dyed. In the operation of dyeing the flesh sides of two of the moistened skins are placed in contact, and are made to adhere by striking them out and scraping them on a flat table, and the dye-stuff is then applied to each skin in succession, by which means it is limited to the grain side. *A light blue* colour may be given to the skin by the use of a mixture of ferrocyanide of potassium and nitrate of iron; a *green* by a combination of the barberry with indigo; a *maroon* by a mixture of archil and ammonia with indigo; a *scarlet* by the action of cochineal, alum, and carbonate of potash; and a rich *purple*, known as *royal purple*, by means of indigo faced with cochineal. Red morocco is usually dyed before it is tanned with sumach.

(1415) 3. *Tawing.*—The thin and delicate skins which are employed in the manufacture of 'kid gloves' are subjected to a different and more careful process than that above described: after they have been washed to free them from blood, and from the salt employed to preserve them from putrefaction, they are anointed on the flesh side with cream of lime, and left for a few days; after which they are washed, and the hair is plucked off. They are then soaked in lime water for a fortnight or three weeks, at the expiration of which time they are carefully smoothed with a whetstone upon a beam. The lime is next removed by soaking the skins in a mixture of bran and water, which has been allowed to become sour; the lactic acid which it contains forms a soluble salt with the lime, and at the same time swells the skin and opens its pores, reducing it to the form of a thin white extensible membrane, technically termed a *pelt*. In this condition it is ready for the operation of tawing, or passing through the *white bath*. Tawing, in fact, consists in preparing the skin with a solution of chloride of aluminum, and subsequently working in a quantity of oily and farinaceous matter.

This white bath is composed of a mixture of alum and common salt, dissolved in water in the proportion of 12 gallons of water to every 100 skins, and from 12 to 18lb. of alum and 2½ to 3lb. of salt: after the skins have been introduced into the mixture the temperature is gradually raised nearly to boiling. When the skins have been soaked for some time in the bath, they are thoroughly kneaded together by placing them in a revolving drum, by which means the liquor is well incorporated with them. They are next washed, first with water, then with a mixture of bran and water, and are dried, after which they are worked with the *paste*. In preparing this paste, about 3 gallons of the alum liquor are mixed with 13 or 14lb. of wheat flour and the yolks of 50 eggs, and in this bath the skins are worked separately, and allowed to remain for 24 hours: at the end of that time they are kneaded together by the action of the revolving drum; they are again dried; they are next dipped in water for a few minutes, and staked or stretched, and are worked upon the board with a softening iron, by which means they are greatly extended in all directions; after which they are stretched upon frames to prevent them from shrinking during the drying. When dry they are tinted, if necessary, with a mixture of whitening and ochre, and are finally polished and ironed.

(1416) 4. *Shamoying.*—The operation of shamoying consists in working into the skin a quantity of oil, which supplies the place of the vegetable astringent, or of the chloride of aluminum, in the processes of tanning and tawing. In preparing the skin for shamoying, the operations of unhairing, and of raising, are the same as in ordinary tanning: a large proportion of shamoyed leather forms what is known as *wash-leather*. This is made from sheepskins, which are split for the purpose, by means of a machine contrived with this view: the grain side of the skin is used in the preparation of hat linings, and for other purposes where but little tenacity is requisite, whilst the flesh side is converted into wash-leather. After the skins have been soaked in bran and water, they are spread out upon a table, and lightly sprinkled with oil; they are then folded into balls, each containing 4 skins, and are beaten for two or three hours in the fulling stocks, with heavy wooden hammers faced with copper; after this they are opened out, again sprinkled with oil, and a second time passed through the fulling stocks, until they cease to appear greasy. They are next hung up in a warm room, where the oil absorbs oxygen; and this oiling and ventilation is repeated two or three times: the skins are then scraped, and scoured with a weak alkaline ley which saponifies the excess of the oil. Afterwards they are washed with water, dried at a gentle heat, and then smoothed and rolled. The thicker leather, known as *buckskin*, is prepared in a similar manner, but the skin used is not split, the grain being removed by means of a knife, which raises a sort of nap upon the surface, but does not cut the leather.

CHAPTER XII.

CHEMICAL PROPERTIES OF SOME OF THE SOLIDS AND FLUIDS OF ANIMAL ORIGIN.

§ I. *Solid Constituents of Animals.*

(1417) THE solid constituents of the animal body differ very materially from those of vegetables. The bony framework of the animal system contains a large proportion of inorganic insoluble salts; and the different tissues, into the composition of most of which nitrogen enters, vary widely from each other in chemical properties. It must not, however, be supposed that any organ of the body consists of any chemical compound in a state even approaching to purity. The complex structure of these organs, consisting as they do of vascular, nervous, and cellular components, independently of the peculiar and proper substance of the organ itself, forbids the possibility of any such simple character in its chemical constitution, although one or two proximate principles may give to it the distinctive features which it offers to the chemist. The bones, the ligaments, the muscles, and the nerves, thus exhibit unmistakeable differences in chemical properties, owing to the predominance in each of certain proximate animal principles.

It will be useful, to consider briefly the chief chemical characteristics of some of the most extensively diffused of these tissues.

(1418) *The Bones* present the same general properties throughout the higher classes of vertebrate animals. When dried at 212°, till they cease to lose weight, they are found to consist of about one-third of their weight of organic matter; the remaining two-thirds being composed principally of phosphate and carbonate of lime and phosphate of magnesia. These facts may be readily verified:—if a bone, freed from fat and periosteum, be suspended in a vessel containing hydrochloric acid diluted with 6 or 8 parts of water, an effervescence will be seen to occur over the whole surface of the bone, owing to the decomposition of the carbonate of lime; in the course of three or four days the salts will have been dissolved out, and the remainder, which still retains the shape of the bone, will be found, after soaking in distilled water repeatedly renewed, to consist of the animal matter, or ossein only. Its rigidity will have disappeared, and it will have become perfectly flexible; but if it be dried, it will assume a semitransparent appearance, resembling that of horn. When boiled for a few hours in water, it will be gradually dissolved, with the exception of a little fat and a few vascular and fibrous shreds, and the solution will gelatinize on cooling, forming a weak glue or size. The solution thus obtained is indeed nearly pure gelatin, and like this substance, is precipitated copiously by tannic acid and by infusion of galls.

The acid solution when neutralized by ammonia deposits the earthy phosphates, which may be separated by filtration, and on adding to the clear liquid a solution of oxalate of ammonia the lime which was contained as carbonate in the bone is precipitated.

Bones may be boiled for many hours in water without undergoing any further change than the separation of a quantity of grease, which rises to the surface of the liquid; but if placed with water in a Papin's digester and exposed to a temperature of about 300°, the gelatin is dissolved and the earthy matters are left, and subside in a disintegrated form.

When bones are distilled in close vessels at a gradually increasing temperature, a large quantity of fœtid, volatile, and tarry matters pass over, accompanied by a large proportion of carbonate of ammonia, and some other volatile alkalies formed on the type of ammonia. The residue in the retort constitutes animal charcoal, and contains the phosphate of lime with a quantity of carbon diffused through it in a very finely divided state. The saline components of the bone may be obtained in an isolated form by calcining bones for some hours in an open fire, when a white ash is left. The composition of bones differs slightly at different ages, and even in different parts of the body of the same animal. The *Teeth* are similar in composition to the bones, but the portion which projects above the gums is encased with a compact hard crust, known as the *enamel*, and which contains but a very small proportion of animal matter :—

Composition of Bones, &c.

	Heintz.			Berzelius.	
				Human.	
	Ox. Femur.	Sheep.	Man. Forearm.	Tooth.	Enamel.
Animal matter .	30·58	26·54	31·11	28·0	2·0
Phosphate of lime	57·67	61·99	59·14	64·3	88·5
Fluoride of calcium	2·69	2·97	2·23		
Carbonate of lime	6·99	6·92	6·32	5·3	8·0
Phosph. of magnesia	2·07	1·58	1·20	1·0	1·5
Other salts . . .				1·4	

The bones of fishes contain a smaller proportion of phosphate of lime than is found in those of the higher orders of vertebrata. The ivory much resembles that of bone; but horny matter in general, whether in the shape of cow-horn, tortoise-shell, whale-bone, the claws of beasts of prey, or the nails of the fingers and toes, the scales of fishes, the feathers of birds, or the wool and hair of animals generally, is of a different composition; it contains but little saline matter, not exceeding 2 or 3 per cent., and does not furnish gelatin when boiled with water at high temperatures under pressure. It becomes soft on the application of heat; a circumstance which is turned to account in the manufacture of common articles in horn, so that they can thus be moulded in some measure to the desired form. Horn is gradually and with difficulty dissolved by alkaline solutions, to which it yields up a portion of sulphur; and on neutralizing the solution with an acid, a precipitate is formed which resembles that obtained from the albuminoid compounds: this precipitate, however, presents properties which are slightly different according to the nature of the source from which it is derived. Horny matter is intermediate in composition between the albuminoid and gelatigenous components of the body. It contains less carbon and more nitrogen and sulphur than the proteic compounds. The following table gives the composition of some of the different varieties of these bodies:—

	Scherer.				Fremy.	
	Epidermis (foot).	Hair (human).	Wool.	Quills.	Turtle shell.	Whale-bone.
Carbon .	51·04	50·62	50·65	52·42	53·6	50·8
Hydrogen	6·80	6·61	7·03	7·21	7·3	7·4
Nitrogen .	17·22	17·93	17·71	17·90	16·4	16·5
Sulphur .	24·94	24·84	24·61	22·47	2·0	25·3
Oxygen, &c.					20·7	

	Mulder.				Crookewit.	Schmidt.
	Nails (human).	Horn (cow).	Hoof (horse).	Fibroin (silk).	Sponge.	Chitin.
Carbon .	50·3	50·0	50·4	48·61	46·51	46·64
Hydrogen	6·9	6·8	7·0	6·50	6·31	6·60
Nitrogen.	17·3	16·3	16·7	17·34	16·15	6·56
Sulphur .	3·2	3·4	3·0	27·55	0·50	40·20
Oxygen, &c.	22·3	23·5	22·9		30·53	

Scherer's analyses (Liebig's *Annal.* xl. 1) are calculated with the old equivalent of carbon, 6·115.

From the foregoing table it will be seen that horny matter differs little from gelatin in ultimate composition, but in its reacsolution of potash, then with alcohol, with water, and with ether. Pure chitin is a white substance, which retains the form of the texture from which it is obtained. It is soluble in concentrated nitric and hydrochloric acids without colouring them, and after neutralizing these solutions with ammonia, it yields a precipitate with infusion of galls. Oil of vitriol gradually dissolves it, and slowly lets fall a black precipitate, whilst acetic acid and acetate of ammonia remain in solution. When distilled it also yields acetic acid and acetate of ammonia; boiling concentrated solution of potash does not affect it. This substance, if it be azotised, is certainly one of the simplest forms of the nitrogenized plastic materials. It presents some points of analogy with vegetable fibre, particularly in the production of acetic acid by its decomposition. Fremy denies the existence of nitrogen in chitin, and assigns to it a composition which would make it isomeric with cellulose, though it does not yield similar products when treated with acids; but the analyses of Lehmann exactly coincide with those of Schmidt.

(1421) *Cartilage.*—The articular extremities of the bones are encrusted with a white elastic opaque horny substance which contains but little saline admixture (from 3 to 6 per cent. of salts), and which by long boiling is gradually dissolved, forming a liquid which on cooling furnishes a tremulous jelly. The transparent cornea, the rings of the trachea, the elastic parts of the ears, nose, and eyelids, and the flexible prolongations of the ribs are also composed of the same material; this substance, however, is not true gelatin, but the modification of it termed *chondrin* (1410).

White fibrous tissue, and the material of which the tendons, ligaments, and inelastic tendinous expansions are composed, consist of a substance which by continued boiling is almost completely dissolved, and a solution of gelatin is formed, which gelatinizes on cooling. *Yellow fibrous tissue* has a different composition: it is insoluble in boiling water, and in weak acids and alkalies, but is readily soluble in hot concentrated sulphuric acid, and in a strong solution of potash. It resists putrefaction for a long time, and possesses great elasticity. Nitric acid forms a yellow compound with it. The yellow fibrous tissue is an advantageous source of leucine when digested with sulphuric acid which has been diluted with 1½ parts of water.

(1422) ***Muscular tissue*** consists principally of fibrin in a coagulated form, but being highly vascular, and containing nearly three-fourths of its weight of water, it is permeated with a fluid consisting partly of blood and partly of substances secreted from it,

(1424) *Inosite* or *Muscle Sugar,* ($C_{12}H_{12}O_{12}$, 4 Aq.)—This interesting body was discovered by Scherer in the juice of the flesh. It may be obtained by the following process:—After separating the kreatine by crystallization, the baryta is removed by the cautious addition of sulphuric acid so long as it occasions a precipitate. The liquid is then filtered, and the free lactic acid separated by repeatedly washing with ether. Alcohol is added to separate the salts; and by gradually increasing the quantity of alcohol, small crystals, resembling those of gypsum, are formed; these crystals consist of inosite. They must be redissolved in water, and recrystallized.

Inosite forms colourless, efflorescent prisms, which lose nearly 17 per cent., or 4 equivalents, of water at a temperature below 212°. The residue has then the composition of grape sugar which has been dried at 212°. At 410° F. the dry mass melts to a colourless liquid, which, on cooling quickly, sets into a crystalline mass. It has a sweet taste, and is freely soluble in water, less so in rectified spirit, and is insoluble in absolute alcohol and in ether. Dilute acids and alkalies, even when boiled with it, produce no change. A solution of inosite, to which caustic potash has been added, dissolves hydrated oxide of copper with a blue colour, but does not reduce it to suboxide when the liquid is boiled. The solution of inosite gives a white precipitate when mixed with one of basic acetate of lead. Inosite is not susceptible of the vinous fermentation, but with chalk and cheese it yields lactic and butyric acids.

(1425) *Chemical Effects of Cooking upon Food.*—A consideration of the chemical constituents of muscular tissue enables us readily to understand the principal changes produced in the cooking of meat. The common processes of cooking have been very clearly explained by Liebig.

The operation of *roasting* consists in the gradual coagulation of the albumen, as the heat penetrates from the surface towards the interior: those parts which are nearest the centre, unless the roasting be continued for a sufficient length of time, do not become hot enough to allow the albumen to coagulate; hence they appear red, juicy, and *underdone* as it is called; the superficial portions become brown, and partially altered in composition, but the greater part of the sapid and saline constituents of the juices contained in the meat are retained, although a certain proportion exudes, and a part of the fat is melted off, and collects below, as *dripping.*

In *boiling* meat the result is somewhat different: when the flesh is placed in cold water, and the heat is gradually raised, the soluble albumen, the soluble salts, and the flavouring portions of the meat (which are contained entirely in the soluble parts) begin to pass out into the water, and the meat gradually becomes impoverished, while the liquid in which it is boiled gains in a corresponding degree in flavour and nutritive qualities—the meat becoming hard, ragged, fibrous, and tasteless at the surface, owing to the loss of its albuminous cement. When the water boils, the heat gradually penetrates the mass of the flesh, and as soon as it has risen high enough to coagulate the albumen which is still left in the central portions the joint is said to be cooked through.

In order to preserve the full flavour of the meat during the boiling, it is necessary to make the water boil before introducing the joint to be cooked, and then to maintain it gently simmering, until every part of the mass has attained a temperature of at least 170° or 180°. By this treatment, the albumen contained in the superficial layer of the meat is suddenly coagulated, and thus offers an obstacle to the free escape of the soluble portions from within; the meat therefore is proportionately richer, whilst the broth suffers to the same extent.

Liebig has introduced an improved method of preparing strong meat tea for invalids, founded upon the foregoing considerations. Lean beef or other meat is minced finely while raw, mixed with an equal weight of cold water, and slowly heated to boiling. After boiling for a minute to coagulate the albumen, the liquid is strained through a cloth, and the fibrous portion exposed to pressure; the broth thus obtained is seasoned with the usual condiments, and furnishes a nutritive soup of excellent flavour, which would gain nothing by longer boiling, but it has little colour.

A still more nutritious broth may be obtained in the following manner:—Take one-third of a pound of raw beef or chicken, mince it very finely, and mix it with 14 ounces of cold distilled water, to which 4 drops of hydrochloric acid and from 10 to 18 grains of salt have been added; digest for an hour, and strain out the meat upon a hair sieve; wash the residue upon the sieve with 5 ounces of distilled water. In this way about a pint of a cold extract of meat is obtained, which may be taken cold, or if warm, it must not be heated above 120° F. The whole of the uncoagulated albumen, one of the most nutritive constituents of the meat, is thus extracted and administered to the invalid; whereas, if the broth be boiled, the albumen becomes coagulated, and is skimmed off and wasted.

The undissolved fibrin when washed once or twice becomes hard and insipid, and is difficult of digestion. The dark colour of soup contributes scarcely anything to its flavour, but custom leads us to associate the idea of strength and flavour with its appearance. The brown tint which long boiling gives, may, as is well known in the kitchen, be supplied by a little burnt sugar, and thus the eye as well as the palate may be satisfied.

The antiseptic power of common salt in preserving meat has been known from time immemorial, but no satisfactory explanation of its mode of action has been given. The process of salting detracts considerably from the nutritive value of the flesh so preserved. When raw meat is salted, the liquid portion speedily begins to ooze out, and to dissolve the salt, forming what is commonly termed *brine*, which is a saturated solution of salt in the juice of the flesh; the meat thus becomes proportionately impoverished of its albumen, and of its sapid and saline components, and at the same time is deprived of its tendency to putrefy.

(1426) *Components of the Brain.*—The chemical knowledge of the components of the brain and nervous system is less satisfactory than that of many of the foregoing substances. It may be remarked that these organs are especially remarkable in a chemical point of view. Fremy, a few years ago, published an investigation upon their composition, which has since been confirmed by Von Bibra in its essential points. The brain contains a large proportion of albumen in the uncoagulated form; but it seems to owe its peculiar properties to the presence of a solid fatty acid, termed *cerebric acid*, which contains phosphorus, and to a liquid, oily acid, called *oleophosphoric acid;* the latter compound also contains phosphorus. In addition to these bodies, cholesterin, and the ordinary fats, stearin and olein, are likewise present.

The human brain contains in 100 parts, about 7 parts of albumen, 5 of the above-mentioned fats, and 80 of water.

Cerebric Acid is a feeble acid, which is met with in the brain partly uncombined, partly united with soda. It is a white solid, which may be obtained in crystalline grains, soluble in hot absolute alcohol and boiling ether, but sparingly soluble in cold ether. It is not soluble in water, but swells up like starch in this liquid: it melts at a somewhat elevated temperature, and at a little above its point of fusion begins to be decomposed. It burns with a characteristic odour, leaving a charcoal, which, from the formation of phosphoric acid, has an acid reaction.

Cerebric acid gave to analysis the following numbers, from which, however, no satisfactory formula can be deduced :—

Carbon	66·7
Hydrogen	10·6
Nitrogen	2·3
Phosphorus	0·9
Oxygen	19·5
	100·0

Oleophosphoric Acid is a greasy oil, which is insoluble in cold alcohol, but readily dissolved by ether and by boiling alcohol. It appears to exist in the brain partially in the free state, but principally in combination with soda, with which it forms a soapy compound. This acid, according to Gobley, is likewise present in the yolk of the egg. Oleophosphoric acid, by boiling it with water, is resolved into olein and into phosphoric acid, which latter remains in solution. The presence of a free acid facilitates this decomposition.

§ II. COMPOSITION AND PROPERTIES OF SOME OF THE MOST IMPORTANT ANIMAL FLUIDS.

The fluids contained in the animal body may be considered in the following order :—

A. Plastic nutrient liquids, under which are included the *blood,* and its tributaries the *chyle* and the *lymph ;* in connexion with which it will be convenient to notice *milk.*

B. Liquids more or less necessary to the process of digestion, including the *saliva,* the *gastric juice,* the *pancreatic fluid,* the *secretions of the mucous membranes,* and the *bile.*

C. Excrementitious matters, comprising the *urine,* the *cutaneous secretions,* and the solid *excrements ;* with which may be noticed *pus,* the product of the suppurative process.

A. *Plastic Nutrient Liquids.*—1. *The Blood.*

(1427) The blood is the most important of the fluids contained in the animal system, since it supplies the material from which the various organs of the body are derived. The remarks which follow refer to the blood of the human species unless otherwise specified.

Since the blood is a fluid which consists of a mixture of a variety of different ingredients, and since it is every moment undergoing changes of the most varied and complicated description, its composition cannot be expected to exhibit the same definite character as that of a crystallized mineral; and yet there is considerable uniformity in the chemical constitution of blood during health. In the vertebrate animals the blood is a somewhat viscid fluid of a red colour, which is more or less bright according to the part of the system from which the liquid has been taken; that from the arteries, or *arterial* blood, being of a florid red: whilst that drawn from the veins, or *venous* blood, is of a dull purple. Blood has a peculiar odour, which differs somewhat in animals of different species. This odour is more strongly developed by the addition of oil of vitriol to the blood. When left to itself, the blood presents the remarkable phenomenon of coagulation, in consequence of which it appears first to become semisolid, and eventually it separates into two portions, one of which constitutes the *solid cruor* or *crassamentum*, and the other the liquid or *serous* portion. This coagulation generally commences in from three to five minutes after the blood has been drawn, and the clot continues to contract for ten or twelve hours. Coagulation is retarded by exposure to a low temperature; it occurs most rapidly at about 100° or 110° F. The coagulation is due to the presence of fibrin, which exists in the blood in a state of solution whilst it is circulating in the living organism, but solidifies shortly after its removal from it: the reason of this coagulation is unknown. During coagulation the fibrin carries with it all the colouring matter of the blood, so that the clot has a deep red hue, and the serum is left colourless or straw-coloured. The reason of this complete separation of the colouring matter is revealed by the microscope. Blood, when exposed to a high magnifying power, is found not to be a homogeneous fluid, but to contain a multitude of small flattened disks, of a deep red colour, tolerably uniform in size in the same animal, but varying in magnitude and shape in different species of animals. These *blood disks*, or *red corpuscles*, consist of a thin cellular envelope, enclosing the true red colouring matter of the blood, and they float in a transparent, nearly colourless fluid, termed the *liquor sanguinis*. In human blood these red corpuscles are circular and slightly biconcave: in most other mammalia the blood disks are also circular; in birds they are elongated and oval, with an elevated centre; and in amphibia they are oval and slightly convex. These observations explain the cause of the complete separation of the colouring matter when the blood coagulates; since the fibrin, in the act of solidification, entangles the red corpuscles in its meshes, and mechanically separates them, just as white of egg does when it is used to clarify syrup by mechanically removing the solid impurities suspended in it. If the blood be whipped with a bundle of twigs during the process of coagulation, the fibrin attaches itself in the form of white elastic filaments to the twigs, while the red particles are separated from it by the agitation. The defibrinated blood is of a deep red colour, and does not coagulate. Blood is prevented from coagulating by allowing it to flow from the vein into alkaline solutions, or into a concentrated solution of many salts of the alkalies, such as nitrate of potash, and sulphate, and acetate of soda. In some cases of sudden death, the blood is also found to have lost its property of spontaneous coagulation. In certain states of the system, owing partly to the slower coagulation of the fibrin, the upper surface of the clot is entirely free from colouring particles, the red corpuscles subside, and leave a stratum of variable thickness and of yellowish colour; to this coating the name of the *buffy coat* of the blood has been given; it is sometimes spoken of as the *inflammatory* crust, owing to its frequent occurrence during inflammatory diseases.

(1428) *Composition of the Blood.*—The following substances have been found as normal constituents of the blood:—Albumen, fibrin, colouring matter or hæmatin, globulin; oleic, stearic, lactic, phosphoric, sulphuric, and hydrochloric acids, in combination with soda, potash, ammonia, lime, and magnesia; minute portions of cholesterin, a small quantity of phosphorized fat (containing phospho-glyceric acid), which has probably a composition similar to that of the fatty matter of the brain. The blood likewise contains in solution, oxygen and nitrogen, derived from the atmosphere, and carbonic acid, which is produced by the reaction of the oxygen upon the constituents of the blood. These gases may be displaced by transmitting a current of hydrogen through the liquid. Lehmann, by passing a current of hydrogen through ox blood till it ceased to expel carbonic acid, and then adding acetic acid without admitting air, and again transmitting hydrogen, has shown, by the expulsion of carbonic acid which then ensued, that recent blood must contain a free alkaline carbonate, in quantity equal to about 0·1628 per cent. of its weight.

The following table, based upon the observations of Schmidt and the analyses of Lehmann, is given by the latter chemist as representing the average quantitative relation of the principal constituents of normal blood. It will be observed that the blood is here regarded as composed of two portions, one consisting solely of the red particles, and the other of the liquid in which these red corpuscles are suspended, termed the *liquor sanguinis*, which consists of the serum holding fibrin in solution:—

Sp. gr. of Blood Corpuscles, 1·0885.	
1000 parts of blood corpuscles contain:—	
Water	688·00
Solid constituents (consisting of)	312·00
Hæmatin	16·75
Globulin and cell membrane	282·22
Fat	2·31
Extractive matters	2·60
Mineral substances (without iron)	8·12
Chlorine	1·686
Sulphuric acid	0·066
Phosphoric acid	1·134
Potassium	3·328
Sodium	1·052
Oxygen	0·667
Phosphate of lime	0·114
Phosphate of magnesia	0·073

Sp. gr. of Liquor Sanguinis, 1·028.	
1000 parts of liquor sanguinis contain:—	
Water	902·90
Solid constituents (consisting of)	97·10
Fibrin	4·05
Albumen	78·84
Fat	1·72
Extractive matters	3·94
Mineral substances	8·55
Chlorine	3·644
Sulphuric acid	0·115
Phosphoric acid	0·191
Potassium	0·323
Sodium	3·341
Oxygen	0·403
Phosphate of lime	0·311
Phosphate of magnesia	0·222

The ash of ox blood contains about 6·84 per cent. of oxide of iron (Lehmann).

The following table gives the results of the average composition of human blood in man and in woman, according to the analyses of A. Becquerel and Rodier:—

		Male.		Female.	
Specific gravity of defibrinated blood			1060·0		1057·5
Of serum			1028·0		1027·4
Water			779·00		791·10
Fibrin			2·20		2·20
Fatty matters,	Serolin	1·60	0·02	1·62	0·02
	Phosphorized fat		0·49		0·46
	Cholesterin		0·09		0·09
	Saponified fat		1·00		1·05
Albumen			69·40		70·50
Blood corpuscles			141·10		127·20
Extractive matters			6·80		7·40
			1000·10		1000·02
Salts,	Chloride of sodium		3·10		3·90
	Other soluble salts		2·50		2·90
	Earthy phosphates		0·33		0·35
Metallic iron			0·57		0·54
			6·50		7·69

The average specific gravity of healthy human blood is from 1·052 to 1·057, but it is liable to considerable variation, principally owing to the colouring matter subsides; it must be collected on a filter, and washed with a solution of sulphate of soda. If the residue upon the filter be now boiled with alcohol acidulated with sulphuric acid, the colouring matter is dissolved. The liquid must be filtered while hot, and a portion of globulin, which has been dissolved, is to be thrown down by the addition of carbonate of ammonia. The red liquid thus obtained is again to be filtered, and evaporated to dryness; after which the solid residue must be digested successively with water, alcohol, and ether, and again be dissolved in alcohol containing ammonia, by which the remaining portions of globulin will be separated in the insoluble form; the solution is then to be filtered and evaporated to dryness; after which everything that is soluble is to be removed by digestion with water. The residue is considered to be pure hæmatin.

Coagulated hæmatin as thus obtained forms a dark mass, which assumes a slight lustre on pressure. It is destitute of odour and of taste, and is insoluble in water, alcohol, ether, and the fatty and essential oils. It is, however, readily dissolved by weak alcohol which has been acidulated with sulphuric or hydrochloric acid: this solution is of a deep brown colour, but it becomes blood red on the addition of an alkali. Water precipitates the acidulated alcoholic solution. Strong acids decompose hæmatin, and extract the greater portion of its iron. Aqueous solutions of the alkalies, both caustic and carbonated, dissolve it freely; when these solutions are boiled, the colour, which is at first bright red, passes through dull red into green. Hæmatin is precipitated completely from its ammoniacal solution in alcohol, by salts of silver, of lead, and of copper. According to Denis, 1000 parts of blood contain 0·56 of metallic iron; so that reckoning the quantity of blood in a man of average stature at 30lb., it would amount to about 120 grains of iron in the blood of the entire human body.

(1430) *Hæmatoidin.*—A remarkable modification of the colouring matter of the blood, to which the name of *hæmatoidin* has been given, has been observed to occur sometimes in old extravasations, and in certain forms of disease. The colouring matter assumes the shape of irregular crystalline fragments, or of perfectly formed transparent red rhombic prisms, which are very sparingly soluble in water; yielding a solution which becomes coagulated at about 145°. Alcohol and nitric acid also produce a precipitate in the liquid. The aqueous solution of hæmatoidin is precipitated by solutions of corrosive sublimate, of subnitrate of mercury, and of sulphate of copper. Acetic acid dissolves the crystals of hæmatoidin readily;

[illegible] produces a liquid of the colour of peach-blossoms; potash does not dissolve them, but changes the colour of the crystals to a deep yellow. Lehmann has pointed out a method by which these crystals may be readily obtained from the blood of various animals, particularly from that of the guinea-pig, the rat, and the mouse. After the serum has been well drained from the clot, the coagulum is to be placed in a cloth, and the greater part of the colouring matter washed out by means of a small quantity of water. The liquid thus obtained is to be filtered, and a current of oxygen transmitted through it for about half an hour: after which a current of carbonic acid gas is to be transmitted through the solution for about 15 minutes. During the latter process the liquid gradually becomes filled with small crystals, which, if allowed to subside, can be separated from the liquid portion. Lehmann found that the formation of these crystals was favoured by the action of solar light, but the exact changes which attend their production are not understood. The crystals obtained from the blood of different animals present differences of form and of solubility. They are generally prismatic, but those of the rat and the mouse are tetrahedral, and are very sparingly soluble, requiring [illegible] parts of water for their solution. The ultimate analysis of [illegible] furnishes results almost identical with those obtained from albumen. The purified crystals from the blood of a dog contained from 0·7 to 0·9 per cent. of ash, more than half of which consisted of peroxide of iron; phosphoric acid was also present in considerable proportion.

Globulin.—The *globulin* with which the hæmatin is combined has already been described (1404) as a compound bearing a strong analogy to albumen; it is contained in a state approaching to purity in the crystalline lens, and it constitutes the most abundant ingredient in the blood-globules.

The combination of globulin with hæmatin, or ***hæmato-globulin***, which is present in the red corpuscles is very readily acted upon by oxygen, and by many other gases, and is concerned intimately with the changes produced in the blood during the process of respiration. Oxygen gas is absorbed by the red corpuscles when suspended in the serum or when dissolved in water, the liquid assuming a brilliant red colour, whilst a disengagement of carbonic acid gas occurs. It is owing to this action of oxygen that the upper portion of the coagulum in venous blood, which is the part most exposed to the action of the air, is of a brighter red than the lower portions of the clot. Carbonic acid is likewise [illegible] red particles; their colour then becomes changed to a dull purple, but the brilliancy of the red hue may be restored by further exposure to the action of oxygen: many saline solutions, such as those of nitrate of potash, also restore the red colour, and a similar effect may be obtained if syrup be added to the liquid. Henle supposes that the change of colour in the red corpuscles by the action of such solutions depends upon alterations in the form and volume of these bodies, in consequence of the solutions producing endosmosis or exosmosis through the cell-membrane which invests the colouring particles, and by increasing or diminishing the transparency of this membrane, causing the colour of the hæmatin to be more distinctly perceptible: but the solution of the colouring matter in water experiences similar modifications in colour, so that the explanation of Henle is not admissible. Sulphuretted hydrogen causes the colour to pass into a dull green, and the red hue cannot be afterwards restored. Protoxide of nitrogen colours hæmato-globulin purple, and oxygen reproduces the scarlet colour in blood which has been thus acted upon. Sulphurous acid, and acid gases in general, darken its colour, which is again restored by oxygen. Admixture with saline solutions also restores the red hue to blood which has been darkened by sulphurous acid. From these facts it is obvious that hæmato-globulin is a compound extremely prone to change under the influence of many reagents.

(1431) 2. CHYLE.—The term *chyle* is applied to the liquid derived from the nutritive portions of the food, which are absorbed from the inner surface of the intestines by a set of vessels, termed the *lacteals*, which pour their contents into one large absorbent trunk, called the *thoracic duct*, by which the chyle, as fast as it is supplied, is emptied into the general current of the circulation. The chyle differs in its qualities according to the nature of the food which has been taken, and according to the situation in which it is collected for examination. When removed from the body, it, in the course of a few minutes, undergoes a spontaneous coagulation, owing to the presence of fibrin. In this respect chyle differs from all the other animal fluids, except the blood and the lymph.

Chyle is an opalescent fluid, of a yellowish white, or pale reddish colour. It has a somewhat saline mawkish taste, and a very feebly alkaline reaction: it is generally more or less milky, from its holding in suspension minute granules, and globules of fatty matter; this milkiness is particularly observable when the food has contained much fat. Chyle, when boiled, generally deposits a few albuminous flocculi. Few satisfactory opportunities have occurred for examining the composition of human chyle. The of which it coagulates in a few minutes after it has been withdrawn from the body, and forms a scanty colourless coagulum. The quantity of fibrin in lymph from the human body, obtained in cases of injury, has been found to be between 0·3 and 0·5 per cent.; in the horse it varied from 0·04 to 0·33 per cent. The quantity of albumen in human lymph is stated to vary from 0·4 to 6·0 per cent., but in the latter case it is not improbable that the lymph was mixed with effused serum.

(1433) 4. Milk.—This important secretion is produced by the mammary gland of the female animal of the order *Mammalia*, after giving birth to young: from the circumstance that the milk constitutes the entire food of the young animal for many months, it presents a high degree of physiological interest in relation to the supply of food, and to the processes of nutrition and of growth.

Milk is a liquid of a well-known yellowish, or bluish white, appearance, which is produced by the presence of a large quantity of oily matter in suspension. It has a sweet taste, a slight but agreeable odour, and a feebly alkaline reaction. When allowed to stand undisturbed for a few hours, the greater part of the fatty matter rises to the surface, and forms the layer which constitutes cream. When viewed by the microscope in a very thin layer, milk appears to be transparent; it contains a large number of highly refracting, transparent, oily globules floating in a transparent liquid; these globules are contained in a very thin investing membrane, which is not visible till the milk is treated with dilute acetic acid. Agitation of the milk with ether does not dissolve the fat, but if a small quantity of potash be added to milk, and it be then shaken up with ether, the fat is completely dissolved, the pellicle which envelopes the globules having been dissolved by the action of the potash.

The object of churning, in the preparation of butter from cream, is to break up mechanically the little sacculi which enclose the oily matter, and thus to facilitate the agglomeration of the fatty particles into masses, and to favour the separation of the liquid constituents which enter into the formation of the *butter-milk*. The more completely the albuminous and caseous matters are washed away, and the more compactly the butter is pressed, the longer may the butter be preserved without becoming rancid, since the caseous matter acts as a ferment, which speedily effects a partial decomposition of the fat. The addition of salt to the butter, by retarding the decomposition of the azotised matter, preserves the fats unaltered for a considerable period.

In addition to oily matter, milk contains two other characteristic ingredients, viz., milk sugar and casein, both of which are held in solution. Albumen is absent from this solution in its usual condition, but it is abundant in the *colostrum*, or milk which is first produced after the birth of the young animal. The quantity of albumen in the colostrum of the cow is so considerable, that it coagulates when heated. The colostrum is denser than normal milk; it has a yellowish colour, and approaches serum in quality. It is worthy of observation that the sugar contained in milk is of a kind which does not undergo alcoholic fermentation, and consequently is not liable to produce an evolution of carbonic acid during digestion, so that distension of the tender stomach and intestines of the young animal from this cause is guarded against.

The salts contained in milk consist of the chlorides of sodium and potassium, of phosphates of the alkalies, and of a certain proportion of soda and potash, which are combined with the casein and confer solubility upon it; in addition to which, phosphates of lime and of magnesia are also found in considerable quantity. These phosphates are essential to the development of the bones of the young animal. A minute quantity of oxide of iron, amounting, according to Haidlen, to 0·47 per cent. of the entire amount of ash, is also found in milk. No sulphates, lactates, or salts of ammonia, are present in fresh milk. The quantity of salts found in cow's milk usually amounts to about 0·7 per cent. In woman's milk it is about 0·2 per cent. The composition of milk varies not only in the different species of animals, but also in the same animal at different periods of lactation, the proportion of butter being especially liable to fluctuation, and being greatly under the influence of diet: it also appears that the milk last yielded during the act of milking is the richest. The following table comprises the results of the analysis of milk in various species of animals, and will give an idea of the general nature of this liquid:—

	Woman.	Cow.	Goat.	Ass.	Sheep.	Bitch.
Water	88·6	87·4	82·0	90·5	85·6	66·3
Butter	2·6	4·0	4·5	1·4	4·5	14·8
Sugar and soluble salts .	4·9	5·0	4·5	6·4	4·2	2·9
Casein and insoluble salts	3·9	3·6	9·0	1·7	5·7	16·0
Sp. gr. varies from . .	1·030 1·034	1·030 1·035	1·036	1·023 1·035	1·035 1·041	1·033 1·036

The spontaneous acidification of milk when kept, and the consequent curdling of the milk, as well as the action of acids nerally, in coagulating milk, and the effect of various neutral
3, lts of the earths upon this liquid, have already been mentioned 59, 1407).

B. *Liquids concerned in Digestion.*

(1434) 1. THE SALIVA.—This secretion is poured out by the arotid and other glands, the ducts of which empty themselves into he cavity of the mouth. Its chief use appears to be to lubricate and noisten the food, and to facilitate the act of deglutition. The aliva varies in composition considerably in different animals. In nan it is an opalescent, somewhat viscid liquid, which froths remarkably on agitation. The quantity of fixed solids which it contains in solution was found by Lehmann to lie between 0·388, nd 0·841 per cent., but it has been observed as high as 1·6 per cent. In the dog the solids amount to about 1·03, and in the horse to 1 per cent. In addition to epithelial particles, and to mucus derived from the mouth itself, the saliva contains a peculiar organic principle, termed *ptyalin,* which resembles albuminate of soda, and which is very prone to putrefaction. Ptyalin constitutes about one-third of the soluble solids of the saliva. It is characterized by its power of converting starch, even in the granular form, into dextrin and into sugar.

The saliva in health has a feebly alkaline reaction; its alkalinity is increased during mastication, and diminishes after the process of digestion is completed. In inflammatory affections of the *primæ viæ* the saliva is, however, generally acid, and the same fact has been observed in various other forms of inflammatory disease. The inorganic constituents of the saliva consist of soda, and salts of potash and soda, with a considerable quantity of the salts of lime, which is deposited from the saliva of many animals (the horse, for example) in the form of crystallized carbonate, when the secretion is exposed to the air and allowed to absorb carbonic acid. It likewise occasionally contains lactates of the alkalies. Saliva also always contains a small quantity of phosphate of lime. This phosphate of lime mingled with a variable proportion of carbonate of lime and of salivary mucus, constitutes those calculous concretions which sometimes form upon the teeth, and are known as *tartar.* Minute quantities of sulphocyanide of potassium are also present in the saliva, as may be proved by the red colour which it yields on the addition of a dilute solution of the perchloride of iron. When sulphur has been taken medicinally, Wright found the quantity of *albumen*, which does not acquire its ordinary properties until after it has been subjected to the action of the pancreatic and biliary secretions.

In preparing this artificial digestive liquid the mucous membrane of the stomach of the pig is generally employed as the source of the pepsin, the most active portion being the glandular layer, extending chiefly along the greater curvature towards the cardia. In the appendix to Lehmann's work (vol. iii. p. 503), it is stated on the authority of Gruenewaldt, who had an opportunity of making experiments upon a woman suffering from a gastric fistula, that the quantity of the gastric juice secreted in twenty-four hours amounted to the enormous quantity of 31 lb.; but the greater portion of this liquid was, of course, re-absorbed by the mucous surface.

In this case the gastric juice was carefully analysed by Schmidt. The following are his results. It had a sp. gr. of 1·020. When heated, it emitted an odour of butyric and propionic acids, and was found to contain in 100 parts:—

Water	954·13
Pepsin	0·78
Sugar, albuminates, lactic, and butyric acid, and ammonia	38·43
Chloride of potassium	0·70
Chloride of sodium	4·26
Potash	0·17
Phosphate of lime	1·03
Phosphate of magnesia	0·47
Phosphate of iron	0·01

No free hydrochloric acid was found in this analysis; but when the stomach of this patient was irritated by introducing peas instead of masticated food, free hydrochloric acid was obtained from the gastric juice, which was secreted unmixed with saliva.

Schmidt found the quantity of free hydrochloric acid in the gastric juice of dogs, when unmixed with saliva, to amount to from 0·245 to 0·423 per cent. Small quantities of chloride of ammonium were also present in it.

(1436) 3. THE PANCREATIC FLUID.—The secretion from the pancreas resembles the saliva in some respects. It has an alkaline reaction, and putrefies rapidly. It possesses the power of saccharifying starch in an eminent degree, so that it appears to assist in an important manner in the assimilation of the amylaceous portion of the food, which is not rendered soluble by the action of the gastric juice. Bernard considers that one of its chief functions is to aid in the assimilation of fatty substances, but the investigations since made in Germany by several careful and experienced observers have thrown some doubt upon the accuracy of this view. It is, however, certain that the pancreatic fluid furnishes a very perfect emulsion when agitated with oil, and it has been found that such an emulsion continues to exhibit the same milky appearance if left at rest for fifteen or twenty hours. Under these circumstances the emulsion, which at first has an alkaline reaction, generally becomes acid, and butyric and other volatile acids are found in the liquid. The liquid from the pancreas generally becomes coagulated when heated; it is one of the few secretions which contains albumen in the soluble form, the proportion of albumen having been found by Tiedemann and Gmelin, in some cases, to amount to 4 per cent. of the entire liquid. They also ascertained the presence of albumen in this secretion in the horse, the sheep, and the dog.

(1437) 4. Mucus.—Those cavities of the body which communicate with the external surface are lined with a peculiar kind of membrane, distinguished as the mucous membrane. The material of which these membranes consist appears closely to resemble albumen in its coagulated state, but it is covered with a pavement of nucleated epithelium cells, which are continually undergoing gradual disintegration and solution. A tough viscid secretion, termed *mucus*, constantly bathes the surface of these membranes. In this secretion the epithelial particles can be traced in different stages of disintegration. The characters of mucus differ greatly with the surface from which it is obtained; but it usually assumes the appearance of a tough glairy semi-transparent mass, which swells up in water, but is not dissolved by this liquid. To the substance which gives it this glairy consistence, the name of *mucin* has been applied. Mucin is turned yellow by nitric acid; but it differs from albumen, since its solutions are not precipitated by corrosive sublimate; it is also not precipitated from its acid solutions by ferrocyanide of potassium until after the acid solution has been boiled. The mucus from the surface of the alimentary canal, and its appendages, is coagulated by acetic acid and by weak acids in general, but it is soluble in alkaline solutions. The mucus from the surface of the urinary organs is dissolved to a certain extent both by acids and by alkalies. Both forms of mucus are immediately coagulated by alcohol, and the secretion presents many characters resembling those of a solution of albumen. Alkaline chlorides are abundant in mucus from the nose; and the phosphates of the alkalies and small quantities of phosphates of the earths are also present.

(1438) 5. THE BILE.—This important secretion is produced from venous blood by the liver, and in most animals provision is made for its accumulation in a sac connected with the gland, termed the *gall bladder*. When taken from this receptacle it constitutes *gall*, or *cystic bile*.

Human bile is a ropy liquid, of a yellowish green colour when concentrated, but of a bright yellow when diluted. It has a peculiar musky odour and a bitter taste. When poured into water it sinks to the bottom, and does not readily mix with it, but it may be mixed with it by agitation, and it then forms a liquid which froths strongly, like a solution of soap. The viscidity of the bile is owing to the presence of a quantity of mucus from the gall bladder, which it holds in solution. Owing to the presence of this mucus the bile is very prone to putrefaction; but if the mucus be got rid of by coagulation with acetic acid and filtration, or otherwise, the bile may be preserved without decomposition for some time.

Ox bile, owing to the facility with which it may be procured, is the variety which has been chiefly examined. It has usually a sp. gr. of about 1·026, and, according to Berzelius, it contains the following ingredients in 100 parts:—

Water	90·44
Biliary and fatty bodies	8·00
Mucus	0·30
Watery extract, chlorides, phosphates, and lactates	0·85
Soda	0·41

No albumen is present in the bile, but its organic constituents contain a small percentage of nitrogen. It also contains sulphur in notable quantity. It is remarkable that the salts found in the bile of salt-water fishes consist almost exclusively of those of potash, while the salts of the bile of fresh-water fishes, and of the herbivora, consist chiefly of those of soda, although, from the circumstances in which the two classes of animals are placed, the opposite results might have been anticipated.

Owing to the facility with which bile undergoes decomposition, the statements of the earlier chemists who examined this liquid were contradictory, and the true nature of the organic constituents of the bile appears to have escaped the sagacity even of Berzelius and of Mulder. Liebig was the first to suggest that the essential component of the bile ought to be regarded as a resinous soap; and the subsequent masterly researches of Strecker have at length removed all doubt respecting the true nature of the biliary secretion.

The result of these investigations has been to show that ox bile may be regarded as a species of soap formed by the combination of two peculiar resinoid acids with soda. Both of these resinous acids (the *glycocholic* and the *taurocholic*) contain nitrogen. The taurocholic acid also contains sulphur, but the glycocholic acid is free from this element. Ox bile also contains, in addition to the mucus of the gall bladder, minute quantities of cholesterin, and a small amount of stearic and oleic acids, united with potash and ammonia. Besides these substances a peculiar colouring matter is found in combination with an alkaline base.

(1439) *Glycocholic Acid;* (*Cholic acid* of Strecker; $HO, C_{52}H_{42}NO_{11}$).—This acid constitutes the principal portion of the resinous matter of ox bile; it forms white voluminous silky acicular crystals, which shrink much in drying; it is sparingly soluble in cold water, more freely so in hot water; the solution on cooling deposits crystals, which have a bitterish sweet taste. Alcohol dissolves it freely, but leaves it as a resinous mass on evaporation: it is very sparingly soluble in ether. The salts which it forms with the alkalies and the earths may be crystallized; they are soluble in alcohol.

Glycocholic acid, when boiled with excess of an alkaline liquid, such as solution of baryta, undergoes a remarkable decomposition: the whole of the nitrogen is separated in the form of glycocine, which remains in the solution, and a new resinoid acid, the *cholic* acid of Demarçay (*cholalic* acid of Strecker), is found in combination with the baryta:—

$$\overbrace{HO, C_{52}H_{42}NO_{11}}^{\text{Glycocholic Acid.}} + HO,BaO = \overbrace{BaO, C_{48}H_{39}O_9}^{\text{Cholate of Baryta.}} + \overbrace{C_4H_5NO_4}^{\text{Glycocine.}}.$$

The elements of glycocholic acid, with those of two equivalents of water, contain the elements of cholic acid and of glycocine; so that the decomposition of glycocholic acid by alkalies is analogous to that of hippuric acid, by acids. If glycocholic acid be boiled with acids it gradually loses water, and becomes converted first into *cholonic acid* ($C_{52}H_{41}NO_{10}$), and then into glycocine, and *choloidic acid* ($C_{48}H_{39}O_9$; 1441), and the latter, by a further loss of water, is ultimately converted into *dyslysin* ($C_{48}H_{36}O_6$).

Solutions of the neutral acetate of lead, of corrosive sublimate, and of nitrate of silver, produce no precipitates in an aqueous solution of glycocholic acid. The salts which it forms with the alkalies are also unaffected by solution of chloride of barium; but they are precipitated when mixed with solutions of the salts of copper, of lead, of iron, and of silver. The silver precipitate is somewhat soluble in boiling water, and crystallizes as the solution cools. Acetic and other acids, when added to the solution of the glycocholates, decompose them, and throw down the acid in the form of a resin. *Glycocholate of soda* ($NaO, C_{52}H_{42}NO_{11}$) may be obtained in crystals by the addition of three or four times its bulk of ether to its alcoholic solution, but it does not crystallize either from water or from alcohol: it fuses easily to a resinous mass. The crystals have a very characteristic form; they consist of six-sided prisms, with the ends obliquely truncated. The *crystallized bile* of Platner consists of a mixture of the glycocholates of potash and soda.

Preparation.—Glycocholic acid is not obtained pure without considerable difficulty. Recent ox bile is evaporated, and the residue is dried at a temperature of 250°; after which it is digested with cold absolute alcohol. The solution thus obtained is filtered, and ether is gradually added; by which means a brown resinous mass is separated. As soon as the liquid has thus deposited most of the colouring matter, it is decanted, and the glycocholates of soda and potash, which are still retained in solution, are precipitated by the further addition of ether. The liquid becomes milky, a further separation of a resinoid substance occurs, after which the glycocholates are gradually deposited in the form of stellate tufts of needles. These crystals must be washed with anhydrous alcohol, containing one-tenth of its weight of ether, and then rapidly dried *in vacuo*. In order to obtain the acid, the crystals must be dissolved in water, and precipitated by dilute sulphuric acid; crystals of glycocholic acid are slowly deposited. This substance, however, is not pure even yet, for a part only of these crystals is soluble in water, scales of a body isomeric with glycocholic acid being left; this insoluble portion has been termed *paracholic acid* by Strecker. If paracholic acid be dissolved in alcohol, the addition of water precipitates it in the form of crystals of glycocholic acid.

(1440) *Cholic acid* of Demarçay, *cholalic acid* of Strecker; ($HO, C_{48}H_{39}O_9$, 5 Aq).—By adding hydrochloric acid drop by drop to the solution of cholate of baryta obtained by boiling glycocholic

Choloidic acid is a resinous, white, friable substance, freely soluble in alcohol, scarcely soluble in ether, and insoluble in water. It reddens litmus, and when treated with sulphuric acid and sugar produces the same reactions as cholic acid. The alkaline choloidates are soluble in alcohol and in water, but they do not crystallize: choloidate of baryta is insoluble in water. These salts are isomeric with the cholates, but do not at all resemble them. Choloidic acid is stated to contain no basic water, but this appears to be doubtful.

Both cholic and choloidic acids, like oleic acid, when distilled with nitric acid yield, by oxidation, the volatile fatty acids of the group $C_nH_nO_4$; acetic, butyric, caproic, œnanthylic, caprylic, pelargonic, and capric acids having been discovered in the results of the distillation by Redtenbacher. Various other oxidized products remain in the retort, among which are oxalic and cholesteric acids (1444), and a crystallizable body termed *choloidanic* acid ($C_{32}H_{24}O_{14}$).

By long boiling with hydrochloric acid, the choloidic acid in turn is decomposed; it loses 3 more equivalents of water, and becomes converted into a neutral resin ($C_{48}H_{36}O_6$), fusible at 284°, and which, from its difficult solubility in ordinary solvents, Berzelius calls *dyslysin.*

(1442) *Taurocholic Acid; Choleic Acid* of Strecker ($HO, C_{52}H_{44}NO_{13}S_2$).—The sulphuretted acid of ox bile is the less abundant of its two components; though it is the principal ingredient in the bile of serpents, of fishes, and of some other animals; it does not appear to have been isolated in a perfectly pure state. It has however been ascertained that it gives rise, by treatment with acids, to cholic or to choloidic acid, and to dyslysin, but instead of glycocine it furnishes a remarkable crystallizable body, which contains all the sulphur of the acid; this substance has been named *taurin* ($C_4H_7NO_6S_2$):—

$$\overbrace{HO, C_{52}H_{44}NO_{13}S_2}^{\text{Taurocholic Acid.}} + 2\,HO = \overbrace{C_4H_7NO_6S_2}^{\text{Taurin.}} + \overbrace{HO, C_{48}H_{39}O_9}^{\text{Cholic Acid.}}.$$

Preparation.—In order to obtain taurocholic acid of tolerable purity, the following method recommended by Heintz may be employed:—To an aqueous solution of ox-bile, neutral acetate of lead is added so long as it occasions a precipitate; the mucus, the oily acids, and the principal part of the glycocholic acid are thus thrown down, and must be separated by filtration. To the clear liquid a solution of subacetate of lead must next be added in small quantities at a time, until the successive precipitates become quite white, and assume a plaster-like consistence, when the liquid must be again filtered, and precipitated by the addition of an excess of subacetate of lead mixed with free ammonia. This precipitate, which consists almost entirely of taurocholate of lead, must be purified by solution in alcohol, and reprecipitation by water; after which it must be decomposed by the action of sulphuretted hydrogen, and the taurocholic acid may be obtained by evaporating the solution, after filtering it to remove the sulphide of lead.

The taurocholates of the alkalies are very soluble in water and in alcohol. They give no precipitate with neutral salts of lead, but with subsalts of this metal slowly deposit a plaster-like compound, which is soluble in boiling water. They yield with sulphuric acid and sugar a violet colour similar to that produced by the cholates.

The bile of most animals yields taurin when treated with the concentrated mineral acids, since the occurrence of taurocholic acid is almost universal in this secretion, but the other resinoid acid varies in different classes of animals; that obtained from the bile of the pig, for example, termed *hyocholic acid*, contains ($HO, C_{54}H_{42}NO_9$). Hyocholic acid yields glycocine when boiled with acids, whilst a new resinoid acid, the *hyocholalic* ($C_{50}H_{40}O_8$), is separated. The compound which hyocholic acid forms with oxide of lead does not possess the fusible plaster-like character which distinguishes the lead salts of glycocholic and taurocholic acids. By long boiling with acids hyocholic acid is converted into glycocine, and *hyodyslysin* ($C_{50}H_{38}O_6$) which is homologous with dyslysin, but contains (C_2H_2) more than the latter compound. Hyocholic acid itself is homologous with *cholonic acid* ($HO, C_{52}H_{40}NO_9$), the resinous acid produced by boiling glycocholic acid with water, which under these circumstances loses two equivalents of water. *Hyocholeic acid* ($HO, C_{54}H_{44}NO_{11}S_2$), the sulphuretted acid of pigs' bile, bears a similar relation in its composition to taurocholic acid that the hyocholic does to glycocholic acid; that is to say, it contains 2 equivalents of oxygen less, and 2 equivalents of carbon more, than taurocholic acid.

(1443) *Taurin* ($C_4H_7NO_6S_2$).—This remarkable substance is readily prepared by freeing fresh bile from mucus by the addition of an acid, and filtering it; the clarified bile is then boiled for some hours with hydrochloric acid; the liquid decanted from the resinous acids is evaporated on the water-bath nearly to dryness, and decanted from the crystals of chloride of sodium which have separated: the mother liquor is then mixed with 5 or 6 times its bulk of alcohol, and the liquid on cooling yields crystals of taurin, which must be purified by recrystallization from water. The crystals of [illegible] assume the form of a six-sided prism terminated by four and six-sided pyramids resembling those of quartz. Taurin is soluble in about 16 parts of cold water; it has a cooling taste; it is not soluble in absolute alcohol or in ether. The mineral acids dissolve taurin without alteration, but do not combine with it, and even when heated with it they do not decompose it. Taurin contains more than 25 per cent. of sulphur, but is a compound of remarkable stability. When burned in the open air it emits abundance of sulphurous acid. Caustic potash dissolves it, and if boiled down with it nearly to dryness, decomposes it, ammonia being evolved abundantly, whilst sulphurous and acetic acids remain in combination with the potash. Hence it appears that the sulphur is already in an oxidized condition. Taurin is isomeric with bisulphite of aldehyd-ammonia, a compound which may be prepared artificially, but which differs in properties from taurin; $C_4H_4O_2, H_3N, 2\,SO_2 = C_4H_7NO_6S_2$. Strecker (*Chem. Gaz.*, 1854, 388) has however succeeded in procuring taurin artificially from isethionate of ammonia. Isethionic acid is prepared by absorbing olefiant gas by means of anhydrous sulphuric acid, and the product thus obtained is dissolved in water; on neutralizing the liquid with ammonia, and evaporating it until crystals are formed on cooling, the isethionate of ammonia $(H_4NO, C_4H_5S_2O_7)$ is obtained. Now this salt contains the elements of taurin and 2 equivalents of water:—

$$\overbrace{H_4NO,\ C_4H_5S_2O_7}^{\text{Isethionate of Ammonia.}} = 2\ HO + \overbrace{C_4H_7NO_6S_2}^{\text{Taurin.}}.$$

On heating the isethionate gradually to 446° F., it loses 11 per cent. of its weight, and the residue when redissolved in water yields by spontaneous evaporation crystals which have the form and properties of taurin from bile. Cloetta has found taurin in small quantity ready formed in the lungs of the ox; he believes it to be the substance termed *pneumic* or *pulmonic* acid by Verdeil.

(1444) *Cholesterin* $(C_{52}H_{44}O_2 + 2\ Aq\,?)$.—This crystallizable fatty body constitutes a never-failing ingredient of healthy bile, though, according to Berzelius, it does not exceed in quantity one part in 10,000 of the bile. It is probably held in solution by the agency of taurocholic acid, which possesses a certain solvent power over cholesterin. It acquires its chief interest and importance from the circumstance that, owing to its extreme insolubility, it cannot be reabsorbed when once deposited, and hence it frequently accumulates in the gall-bladder, and forms the principal ingredient in the most common variety of *gall-stone* or biliary calculus. Cholesterin is found also as a normal constituent of the blood; it is present in the brain in considerable quantity; it is also a constituent of the yolk of the egg, and in small proportion is a very frequent component of serous and fibrous exudations. It appears also to be always present in pus.

Preparation.—Gall-stones which contain cholesterin have a crystalline structure, and fuse on the application of heat, and they often have a specific gravity less than that of water. Such calculi furnish the best source of cholesterin. In order to obtain it from them the powdered gall-stones should be boiled in alcohol; the solution as it cools deposits characteristic rhombic plates of cholesterin, which, after one or two recrystallizations, is obtained in a pure state.

Cholesterin is nearly insoluble in water; ether dissolves it abundantly. When the ethereal solution is mixed with half its volume of alcohol and left to spontaneous evaporation, regular crystals are deposited; they contain about 5 per cent. of water: when heated to 212°, the crystals become opaque, and the water is expelled. Cholesterin fuses at 293°, and becomes crystalline on cooling; it may be distilled at a temperature of 660° without decomposition; but at a somewhat higher temperature it is partially decomposed. In the open air it burns with a smoky flame. The alkalies do not act upon it. Concentrated sulphuric acid decomposes it by removing water and forming a mixture of three isomeric hydrocarbons ($C_{52}H_{42}$) termed *cholesterilin*, which are distinguished by the letters *a*, *b*, and *c*. Long boiling of cholesterin with nitric acid converts it first into a resinous mass and then decomposes it, producing, amongst other bodies, *cholesteric acid* (HO, $C_8H_4O_4$), which assumes the form of a light-yellow deliquescent substance, of an acid and bitter taste; it is readily soluble in alcohol. According to Redtenbacher, the production of acetic, butyric, caproic, and oxalic acids, also accompanies the formation of cholesteric acid.

Biliary calculi are often found in the gall-bladder in large numbers; they vary a good deal in appearance and shape: in some cases they are nearly semi-transparent, and crystallized throughout, at other times they are strongly tinged with the colouring matters of the bile. Occasionally the cholesterin is deposited upon a nucleus of phosphate of lime, or of biliary colouring matter in combination with lime.

In some species of oriental goats, concretions, called *bezoars*, of a brownish-green colour, are occasionally found in the stomach and intestines; they contain a substance termed *lithofellic acid* [illegible] ich a good deal resembles cholesterin in appearance. This body crystallizes in six-sided prisms, or in small rhombic prisms, with an oblique terminal face. It is insoluble in water, sparingly soluble in ether, but freely soluble in hot alcohol and acetic acid. At 400° it fuses, and if heated to a little beyond this it is converted into a resinous mass, the fusing point of which is reduced to about 230° F. If this resin be redissolved in alcohol it is again converted into the crystallizable acid. Lithofellic acid burns with an agreeable odour and a white smoky flame. It combines with the alkalies and forms soluble salts; the salts of lead and of silver are insoluble, and soften in hot water. Lithofellic acid is distinguished from cholesterin by its higher melting point and by its ready solubility in solutions of the caustic and carbonated alkalies, and in acetic acid.

The following table will assist in indicating the relations which subsist between the most important of the numerous compounds obtainable from the bile:—

Glycocholic acid	$C_{52}H_{43}NO_{12}$	Hyocholic acid	$C_{54}H_{43}NO_{10}$
Cholonic acid	$C_{52}H_{41}NO_{10}$		
Cholic acid	$C_{48}H_{40}O_{10}$	Hyocholalic acid	$C_{50}H_{40}O_{8}$
Choloidic acid	$C_{48}H_{39}O_{9}$		
Dyslysin	$C_{48}H_{36}O_{6}$	Hyodyslysin	$C_{50}H_{38}O_{6}$
Taurocholic acid	$C_{52}H_{45}NO_{14}S_{2}$	Hyocholeic acid	$C_{54}H_{45}NO_{12}S_{2}$
Cholesterin	$C_{52}H_{44}O_{2}$	Lithofellic acid	$C_{40}H_{36}O_{8}$
Taurin	$C_{4}H_{7}NO_{6}S_{2}$	Glycocine	$C_{4}H_{5}NO_{4}$

(1445) *Colouring Matters of the Bile.*—If an alcoholic solution of bile be filtered through a column of animal charcoal, it runs through nearly deprived of colour; but the colouring matter of the bile has never been isolated in a state of purity. There appear to be two modifications of it, one of them is brown, the other green: the latter is abundant in the herbivora; it forms the *biliverdin* of Berzelius, who considers this green pigment to be identical with the chlorophyll, or green colouring matter of vegetables. It is insoluble in water, but is taken up by alcohol and by ether. In human bile the brown pigment preponderates; it has been termed *cholepyrrhin.* This brown colouring matter has a strong tendency to combine with the alkalies and the earths; with the latter it forms compounds which are insoluble in water and in alcohol. The brown colouring matter of the bile is very rapidly altered by reagents. The changes of colour produced in it by the action of nitric acid have been proposed as one means of detecting the presence of bile in certain cases, as, for instance, when it occurs in urine: when a solution containing this colouring matter is mixed with nitric acid, the colour becomes at first green, then the diet and state of health of the individual, but it usually averages about 1·020. The quantity passed during the twenty-four hours also varies with the quantity of liquids taken, but on an average it may be estimated at forty ounces. Urine, when left to itself, speedily begins to undergo change. In most cases it first exhibits an increase of acidity, as Scherer has shown; but after standing for a few days it begins to putrefy, and then acquires a powerful alkaline reaction and an ammoniacal odour, owing to the conversion of the urea into carbonate of ammonia. This alkaline decomposition of the urine sometimes takes place within the bladder, particularly after injuries to the spinal cord attended with paralysis of the lower part of the body. The mucus of the bladder appears to act as a ferment upon the urine, and has a large share in producing this decomposition of the urea.

Composition.—Urine contains among its components, urea, uric acid, hydrochloric, sulphuric, and phosphoric acids, in combination with potash, soda, lime, magnesia, and traces of ammonia. It also always contains a little vesical mucus, together with some other ill-defined azotised principles. In addition to these bodies, Stædeler has noticed the presence of minute quantities of certain acids homologous with the carbolic and with oleic acid. The bodies contained in the urine are mainly the products of oxidation, occasioned by the action of respired air upon the nitrogenized tissues, and upon the sulphur and phosphorus which they contain. The following table represents the average composition of healthy human urine:—

				In 100 parts of solid matter.
Specific gravity			1·020	
Water			956·80	
Solid matters, 43·2	Organic matters, 29·79.	Urea	14·23	33·00
		Uric acid	0·37	0·86
		Alcoholic extract	12·53	29·03
		Watery extract	2·50	5·80
		Vesical mucus	0·16	0·37
	Fixed salts, 13·35.	Chloride of sodium	7·22	16·73
		Phosphoric acid	2·12	4·91
		Sulphuric acid	1·70	3·94
		Lime	0·21	0·49
		Magnesia	0·12	0·28
		Potash	1·93	4·47
		Soda	0·05	0·12
			999·94	100·00

human urine is greatly increased. The question of the source whence uric acid is derived is full of interest, especially to the practical physician, since its morbid prevalence is intimately connected with some of the most distressing maladies which afflict the human frame, such for example as gout, rheumatism, and certain forms of calculous concretions from the urine. In some kinds of gout, uric acid is developed and retained in the system, chiefly in the form of urate of soda, in the neighbourhood of the smaller joints, such as those of the fingers and toes, and the wrists, forming deposits commonly known as chalk stones. The system is in these cases loaded with lactic and acetic acids, the latter of which is thrown off abundantly in acid sweatings. Dr. Garrod, in cases of gout, has invariably found uric acid to be present in the blood, and he has also frequently detected it in the blood in Bright's disease: it has been found occasionally in healthy blood. Uric acid is likewise discovered without difficulty in the blood of animals from which the kidneys have been extirpated.

The constitution of the urine is found to vary at different times of the day. That voided in the morning, for example, after the lapse of a considerable interval without the ingestion of food, is the result chiefly of chemical actions going on within the body itself, and is furnished by the decomposition of the tissues. Such urine has a very different composition from that passed in the evening, into which various bodies have been absorbed directly from the stomach. The nature of these bodies necessarily varies with that of the food, which also materially influences the quantity both of uric acid and of urea. With reference to this point, it was found by Lehmann in a series of experiments upon his own person, that after restricting himself to an animal diet for several days, he excreted daily 821 grains of urea, and 21·6 grains of uric acid. After an exclusively vegetable diet for a similar period, the quantity of urea in twenty-four hours amounted to 348 grains, and the uric acid to 15·4 grains; and after subjecting himself to a diet from which nitrogen was as far as possible excluded, the quantity of urea fell to 237 grains. When a highly azotised diet was taken, the same observer found that five-sixths of the entire quantity of nitrogen taken in the food was eliminated from the system in the form of urea. With an ordinary mixed diet the urine amounted to 37·3 ounces daily, and it contained 501 grains of urea and 18·2 of uric acid. These quantities of urea and uric acid are somewhat higher than the average of that excreted by the healthy adult. The quantity of sulphuric acid in the urine is also mainly influenced by the proportion of azotised food taken; this acid indeed, appears to be derived principally from the sulphur contained in the protein compounds assimilated from the food. When a mixed diet was used, Lehmann found the quantity of sulphuric acid excreted daily to amount to 108 grains; with an animal diet it rose as high as 165 grains, and when a purely vegetable diet was consumed, the quantity of sulphuric acid excreted in the twenty-four hours fell to 90 grains. Many substances when taken into the stomach pass off unchanged by the kidneys, especially those which are of a saline nature, such, for instance, as iodide of potassium, and ferrocyanide of potassium: these salts may be commonly detected in the urine within half an hour after they have been swallowed.

(1448) *Urinary concretions.*—Although the urine in a healthy individual usually remains clear and transparent, even after it has cooled, it not unfrequently, under the influence of disturbed health, deposits more or less abundantly some of its less soluble constituents; these deposits in some cases assume the form of a light flocculent powder, at other times they appear in more compact grains, which constitute the different forms of gravel, and in other instances they collect into larger masses, and give rise to urinary calculi.

The most common urinary sediments are those which contain uric acid. When the uric acid is uncombined with bases it often appears in small crystalline masses resembling grains of coarse sand, constituting the ordinary variety of *red gravel*, which consists of uric acid tinged with the yellow colouring matter of the urine: this sediment, if examined under the microscope is usually seen to possess the form of rhomboidal crystals, the edges of which are frequently rounded. In other cases the acid is found in the form of a light-brown amorphous sediment consisting of urate of ammonia. Both these sediments, and especially the latter, are materially influenced by diet: excess of any kind, particularly in animal diet, drinking too much of acescent fermented liquors, over anxiety, exposure to cold, damp weather, and want of exercise, very frequently produce an increased excretion of uric acid, and cause a deposit of the urates of soda and of ammonia even from persons in health. In those suffering from an habitual deposit of red gravel, an animal diet frequently aggravates the disease in a remarkable manner. On the other hand it has been observed that uric acid is less abundant in the urine in summer, and is generally diminished after copious sweats. Lehmann states that the formation of uric acid calculi is unknown in tropical climates.

When *phosphoric acid* is present in the urine in excess, it sometimes shows itself in the form of a white sand, which is usually crystallized, and consists of phosphate of magnesia and ammonia: but occasionally the deposit is amorphous. These two varieties of sediment constitute *white gravel;* they are attended almost constantly by an alkaline state of the urine.

The principal varieties of urinary *calculi* as distinguished from *sediments* are the following:—1. Uric acid; 2. Urate of ammonia; 3. Oxalate of lime; 4. Phosphate of lime; 5. Phosphate of magnesia and ammonia; 6. Fusible calculus (a mixture of the two preceding ones); 7. Xanthic oxide; and 8. Uric oxide. Urinary calculi are in many cases formed upon some foreign body as a nucleus, such as a clot of blood or a crystal of any kind.

1. *Uric acid* calculi are usually of a brownish-red or fawn colour: they have a smooth or finely tuberculated surface; when sawn through they are generally found to be composed of concentric laminæ, and are somewhat crystalline. If a fragment of such a calculus be heated before the blowpipe, it is consumed, emitting a peculiar animal odour, and leaving only a minute white ash. This variety of calculus is soluble in a solution of potash, and uric acid is precipitated in white silky crystals on supersaturating the solution with an acid. If a fragment be heated on a slip of glass with nitric acid, it is dissolved with effervescence, leaving an orange-coloured residue which is rendered of a beautiful pink or crimson by the addition of a drop of ammonia, after which the addition of a solution of potash developes a magnificent purple.

2. The *urate of ammonia* calculus is very rare: it is usually clay-coloured, and smooth; and is deposited in fine concentric layers of an earthy appearance. It is more soluble in water than the preceding variety, and is dissolved with extrication of ammonia when heated with a solution of potash; in other characters it resembles uric acid.

3. *Oxalate of lime* often occurs as a morbid ingredient of urine. The *mulberry calculus* consists of this substance: this form of concretion has usually a deep brown colour; it is deeply tuberculated and rough, and is very dense and hard. When heated before the blow-pipe, it first blackens, and then, if exposed to a moderate red heat, it burns to a white ash consisting of carbonate of lime, which is dissolved by acids with effervescence; but if it has been more strongly heated, the ash is alkaline to test paper, and consists of pure lime. The finely powdered calculus is soluble in nitric and hydrochloric acids, but it is insoluble in acetic acid. Concretions of oxalate of lime have been found in some of the lower animals, as well as in man. Prout considered its occur-

[illegible] in the urine to be due to faulty assimilation of saccharine matters, but the conditions under which it is produced are not well ascertained.

4. Phosphoric acid when combined with lime forms a rare species of calculus, the *bone earth calculus* ($3\,CaO, PO_5$) which is usually of a pale brown colour with a very smooth surface, and is regularly laminated in its texture; these laminæ are often deposited [illegible] radiating from the nucleus. The bone earth calculus is infusible before the blow-pipe; it is readily dissolved by hydrochloric acid, and the phosphate of lime may be precipitated from the solution in a gelatinous state by the addition of ammonia.

5. Another form of phosphatic calculus consists of the phosphate of magnesia and ammonia ($H_4NO, 2\,MgO, PO_5$). It is not unfrequent, and is spoken of by the older writers as *triple phosphate.* It is white, brittle, and more or less crystalline in structure; it is seldom laminated, and its surface is uneven. It fuses with difficulty before the blow-pipe, emitting an odour of ammonia: dilute acids dissolve it readily, and the solution when neutralized with ammonia deposits it again in a crystalline form.

6. A third species of phosphatic concretion is the *fusible calculus,* which consists of a mixture of the two preceding varieties. It is of frequent occurrence, and forms white friable masses which are rarely laminated, and often acquire a large size. This form of calculus fuses readily before the blow-pipe; it is soluble in dilute acids, from which oxalate of ammonia separates lime, and pure ammonia throws down phosphate of magnesia. When the occurrence of phosphatic deposits is habitual, it always indicates a state of constitution severely disordered. Occasionally these phosphates are secreted from the lining membrane of the bladder in large quantity, forming a mortar-like mass of concretions. The earthy phosphates are introduced into the system in considerable quantity in the seeds of the cerealia: beer contains so much phosphate of magnesia, that, on adding ammonia, the double phosphate of ammonia and magnesia is precipitated in abundance.

The phosphates are also common ingredients of calculi in herbivorous animals: in many instances they appear to be deposited from the urine simply from the development of free alkali, either owing to the decomposition of the urea, or to excess of alkaline matter introduced from without.

Compound calculi are not unfrequent; they are formed of a succession of laminæ, composed of one or other of the foregoing varieties. For instance, uric acid, oxalate of lime, and fusible calculus sometimes occur in successive layers in the same calculus.

7 and 8. The characters of the rare calculi containing the compounds known as *xanthic* and as *cystic oxide* have been already described (1396).

The further prosecution of this subject belongs more properly to a work devoted to pathology than to one treating of general chemistry. For the microscopic appearances of the various substances deposited from the urine, the reader is referred to Golding Bird's treatise on urinary deposits, and to Beale's treatise on the microscope.

(1449) The urine in disease undergoes other important modifications in its constitution: two only of these will be adverted to on the present occasion.

Diabetic Urine.—In the disease termed *diabetes* the urine is found to contain a large quantity of grape sugar, which is entirely wanting in the healthy state of the secretion. The source of this sugar lies in the faulty digestion of the food. The sugar appears to be absorbed directly from the alimentary canal into the blood, and is thence separated unchanged by the kidney. Dr. Percy has found that sugar when injected into the blood is separated in an unaltered form in the urine. The quantity of sugar which is excreted in twenty-four hours by patients suffering from diabetes is frequently enormous, amounting in some cases to upwards of 1¾lb. of solid glucose. The proportion of sugar excreted in this disease, is greatly under the control of the diet; substances which contain much amylaceous or saccharine matters, such as bread and potatoes, always occasion the secretion of a larger quantity of sugar: under the use of opium, and an animal diet, the saccharine matter is very considerably diminished.

If sugar be present in the urine, its presence may be inferred by the employment of Trommer's test, in which the reducing action of glucose upon the salts of copper is taken advantage of. The urine is first rendered strongly alkaline by the addition of a solution of potash, a few drops of sulphate of copper in solution are added; on agitation, the hydrated oxide of copper, which is at first precipitated, is redissolved; and upon boiling the liquid, the yellow hydrated suboxide of copper, which is speedily converted into the red anhydrous suboxide, is thrown down. If this reaction does not occur, no sugar is present. Since, however, other bodies besides sugar exercise a similar reducing influence on the oxide of copper, the presence of sugar should be further confirmed by the test of fermentation. In order to apply this test, a small quantity of yeast is added to a portion of the urine, which is placed in an inverted tube over mercury, and exposed to a temperature of 80°;

ately diminished. In fact processes occur upon the surface of the skin, which resemble those both of the kidney and of the lungs: thus, like the kidneys, the skin excretes nitrogen and acid substances as well as the chlorides; and, like the lungs, it separates large quantities of carbonic acid and aqueous vapour. The actions of the skin, and of the kidneys and lungs, are, therefore, though to a very limited extent, vicarious; and when the functions of the skin are seriously interfered with, it usually happens that derangements more or less serious, either of the kidneys or of the lungs, occur.

(1451) 3. Solid Excrements.—After the chyle has been absorbed into the system during the gradual passage of the mixed constituents of the food through the intestinal canal, those parts which are destined to become excrementitious gradually acquire a fæcal odour, and are at length rejected from the body. The composition of these excrementitious matters necessarily exhibits great variations, which depend mainly upon the nature of the food taken. Berzelius found a specimen of human excrements which he examined, after the use of an ordinary mixed diet, to contain three-fourths of its weight of water, the rest consisting of biliary matter and alimentary debris. A large quantity of phosphates of lime, and of magnesia, and other insoluble salts of the food are obtained on incinerating the dried residue. Playfair found in a sample which he examined about 15 per cent. of nitrogen in the dry residue, and 45 per cent. of carbon. The ratio which these numbers bear to each other does not differ much from that which represents the proportion of the same elements in fresh muscle, which likewise contains three-fourths its weight of water. According to Liebig the total average weight of fæculent matter in its recent state excreted by a healthy adult in twenty-four hours amounts to 5½ ounces. The offensive odour of fæcal matter is due to some intermediate products of oxidation. These odorous substances have not been accurately examined, but they may be produced artificially by fusing casein with hydrate of potash, as in the preparation of tyrosine (1380). This odour is of a different nature and of a more putrid character when the quantity of bile secreted is below the usual amount.

Dr. W. Marcet states that, from healthy human excrement, he has obtained a peculiar crystallizable principle which, from its origin, he terms *excretine;* he found it to contain nitrogen and sulphur; it has a feebly alkaline reaction; it fuses at a little above 200°, and is insoluble in water and in a solution of potash, but is readily soluble in ether. No analysis of this body, however, has been published. He has also extracted from the excrements a fusible olive-coloured fatty body termed *excretolic acid;* but has not succeeded in an attempt to determine its composition.

(1451 *bis*) 4. PUS.—This is a liquid which is never met with excepting as a product resulting from actions excited by injury, or by disease. When the suppurative process is going on favourably, pus forms a thick, opaque, yellowish fluid, which, when examined by the microscope, is found to consist of a transparent liquid, in which a large number of corpuscles are seen to be floating. These corpuscles are larger than the red corpuscles in human blood; they consist of a granular cell membrane enclosing a viscid granular matter, and a nucleus which adheres to the membrane. Pus generally has a feebly alkaline reaction. The fluid portion holds a considerable quantity of albumen in solution, and closely resembles ordinary serum. The pus globules contain a considerable proportion of fat, and of cholesterin. *Pyin* is the name which has been given to an albuminoid substance sometimes found in pus; it is soluble in water, but is precipitated by acetic acid and by a solution of alum. The dried residue of pus yields a large amount of salts; in the experiments of Lehmann the saline constituents exceeded 12 per cent. of the total dry matter: the proportion of phosphates and of salts of potash was very considerable.

CHAPTER XIII.

ON THE NUTRITION OF PLANTS AND ANIMALS.

§ I. *On the Nutrition of Vegetables.*

(1452) ORGANIZED beings have been arranged under the two great divisions of *plants* and *animals;* and although the lowest genera in each division approximate so closely that it is difficult to decide where one division begins and the other ends, yet in their general [illegible] they are not only widely different, but even opposed to each other in the functions which they discharge in the economy [illegible] the operations of the plant being complementary to those of the animal in the nicely adjusted balance of organic life each affording support and nutriment to the other. The principal functions of the plant and of the animal may be contrasted thus :—

Plants	*Animals*
Decompose water and carbonic acid.	Produce and evolve water and carbonic acid.
They evolve oxygen.	They absorb oxygen.
They absorb and assimilate nitric acid and ammonia.	They produce and emit urea, and other azotised compounds which yield ammonia.
They are fixed in the soil.	They possess the power of locomotion.
They have no power of voluntary action.	Their actions are under the control of the will.
Their growth is continuous, and there is no absorption of matter once deposited.	Their growth, and the absorption of deposited matter in the adult, go on *pari passu*.

Two important functions have been allotted to the vegetable creation, one of which consists in the elaboration from inorganic matter of the various materials necessary to the support of animal life; the other consists in the removal of carbonic acid from the atmosphere, the plant retaining the carbon and fixing it in its tissues, whilst the oxygen is restored to the air. These wonderful changes are produced by the actions of the vegetable cell; each cell possessing a separate and independent power, by means of which it is enabled to assimilate new matter; from this assimilated matter it produces new cells, and these in like manner multiply and produce innumerable other cells. These successive developments of vegetable cells may be readily watched under the microscope in the case of the growth of the globules of yeast (954). The compounds produced in the yeast globules are cellulose, which forms the cell membrane, and the internal substance, which contains a body allied to albumen. The plant-cell in the case of yeast does not elaborate the azotised product, but assimilates it from the solution in which it grows; there is, however, no doubt that albumen is elaborated in other instances by the vegetable cell :— in the wheat plant, for example, the azotised gluten is stored up in the seed, and in this case it can only be derived from the inorganic materials of the soil and of the atmosphere.

But the mere existence of an organized structure, even when animated by the vital force, is not sufficient to produce these results of vital activity. It is necessary, in addition, that the plant be exposed to a temperature ranging between 40° and 90°, and to a certain degree of moisture. In the higher manifestations of plant life, solar light is also essential. If at any time the temperature fall so low that the plant is frozen, its vitality is destroyed, and the delicate structures of the tissues are impaired by the soli-

dification and forcible expansion of the juices which they
Life is also destroyed not less completely by exposur
organism to a temperature of 212°, or even to one con
below that point. The higher orders of plants require
full development that they shall be rooted in a congenial
be supplied freely with air and moisture.

A plant in a state of health is continually undergoing incr
increase, however, may either be checked or facilitated by m
the circumstances under which it is placed. In order that th
of regulating this development may be more fully underst
necessary to examine what the materials are of which this
consists, and whence they are supplied. In all plants t
two distinct sets of substances present; one of these is o
its nature and is represented by sugar, starch, wood, albu
the other is inorganic, and is represented by the various sa
in the ashes of plants. The materials from which the
pounds are formed must, therefore, be supplied in some
other to the growing plant; in fact, they constitute its fo
periment has, however, proved that the form in which these
are presented to the plant is by no means unimportant,
elementary bodies, with the exception of oxygen, are never
assimilated; they must previously have entered into com
in some form or other. The compound constituents of th
plants are supplied from two sources, the atmosphere and
Those furnished by the atmosphere consist chiefly of carbo
water, ammonia, and nitric acid; while the saline compoun
vary with the nature of the plant, are derived from the so
out these different articles of food, viz., carbonic acid, wa
monia, and the salts of the soil, plants could no more co
exist than animals could do if deprived of their natural nu

The root of a plant may be considered as its mouth,
leaves as its lungs. When a shower of rain descends thr
air, it carries with it all the soluble matters which that p
the air contains; these soluble matters consist chiefly of
acid, with minute quantities of carbonate and nitrate of a
The carbonic acid, as we have already stated, is abunda
nished by the processes of respiration in animals, by com
and by a variety of other sources. The ammonia is f
mainly by the putrefaction and partial oxidation of animal
getable matters, and is present in the air, in a quantity
minute than carbonic acid, but still in appreciable quantiti
Nitric acid is produced whenever a flash of lightnin
thro [illegible] air, and this compound is generated ev

silent discharges of electricity take place. Every shower of rain which falls to the earth, thus dissolves and carries with it food for vegetation; charged with these nutritive materials, the water percolates through the soil, from which it takes up small quantities of soluble salts. It thus arrives at the spongioles of the roots, where it is absorbed and carried up by the ascending current of sap, to the leaves, and to the remotest extremities of the branches,* where, under the influence of some azotised matter, and of the solar light, the carbonic acid undergoes a remarkable change: a portion of the water likewise experiences decomposition, in consequence of which, oxygen gas, mingled with a quantity of nitrogen varying from one-half to one-tenth of the bulk of the oxygen, is given out. Supposing that this decomposition be effected upon carbonic acid and water, in the proportion of one equivalent of each of these compounds, a substance would be formed, having the same ultimate composition as fructose, or fruit-sugar; $CO_2 + HO - O_2 = CHO$, or $12\,(CO_2 + HO - O_2) = C_{12}H_{12}O_{12}$.

Sugar indeed, appears to be the basis or foundation of organic matter in general, and from it all the varieties of organized products might be obtained, by the addition or subtraction of water, oxygen, and ammonia. If fructose ($C_{12}H_{12}O_{12}$) be deprived in the plant of 2 equivalents of water, starch or cellulose is the result, and starch may again be brought into solution when necessary for the plant, by the action of diastase, or of some principle which acts as a ferment, and enables it to resume the water which it had lost. The latter change actually takes place during the germination of seeds, which, when moistened, swell and absorb oxygen, whilst carbonic acid is emitted, and the starch, under the influence of diastase is converted into sugar, in which form it serves as food for the young plant. If the growth of the seed be checked at a particular stage by suddenly raising the temperature, the greater part of the starch will be found to have disappeared from the seed, and its place will have been taken by sugar; these being in fact the changes which occur in the process of *malting* (940). But, if germination be allowed to proceed, the starch and the sugar gra-corresponding to oil of turpentine, and forming the basis of many of the resins; $20\,CO_2 + 16\,HO - 56\,O = C_{20}H_{16}$.

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* Although it has been stated that the principal supply of carbonic acid is furnished to the plant in solution in water which is absorbed from the soil by the roots, it must not be forgotten that the leaves also present powerfully absorbent surfaces, and, like the lungs in animals, not only minister to the respiration of the organism, but are frequently the inlet of a variety of substances which are capable of assimilation, as well as of those that are not so. Carbonic acid, in particular, is absorbed by the leaves with great rapidity, as has been shown by the experiments of Pepys and others.

The complicated azotised principles may be also traced in theory to grape-sugar; thus:—

$$3\,\overbrace{(C_{12}H_{12}O_{12})}^{\text{Fructose.}} + 4\,H_3N = \overbrace{C_{36}H_{27}N_4O_{12}}^{\text{Protein.}} + 21\,HO + O_3.$$

These equations have been given with the view of pointing out the simple relations of sugar to the various organic acids, and not with any intention of asserting that the changes which they indicate actually take place in the form thus represented, though it is obvious that some such changes must occur. Sugar or gum, and starch or ligneous fibre, are amongst the most abundant and generally diffused vegetable productions, and it is very probable that these bodies may furnish the materials from which the various vegetable acids and other simpler compounds of vegetable origin are obtained: but if this hypothesis be doubted, there is no difficulty in tracing these acids and the other bodies to the carbonic acid and water upon which the plant operates. For instance, oxalic acid might be produced from carbonic acid and water by the following changes; $4\,CO_2 + 2\,HO - O_2 = 2\,HO, C_4O_6$. In the case of malic acid, the changes might be the following: $8\,CO_2 + 6\,HO - O_{12} = 2\,HO, C_8H_4O_8$; and so on with the others.

It is impossible in the existing state of our knowledge, to trace the cause, or even the exact nature, of the changes produced in the various fluids which circulate in the plant or in the animal. The theory which has the strongest apparent analogies in its favour, is that by the presence of some albuminous ferment, analogous to diastase, or to synaptase, an elimination of various compounds takes place in particular organs, just at those points where these ferments are deposited. It is further supposed that the same complex organic fluid is capable of undergoing changes differing with the nature of the substance which excites fermentation, and that hence it happens, that the same fluid may deposit in different tissues, secretions possessed of very different qualities (939). The substances thus produced must necessarily be complementary to each other: that is to say, the product of secretion and the altered fluid which furnishes it, taken together, must contain the same elements as the original substance from which they were produced. It must, however, be confessed that the foregoing hypothesis affords no explanation of the manner in which compounds previously existing in the circulating fluid, as urea is known to do in the blood, are separated from it by the ordinary operation of secretion.

material which, like peroxide of manganese, furnishes oxygen, formic acid is one of the products. In like manner, under the influence of potash, the natural fats and oils are decomposed into fatty acids and glycerin. Analogous changes may be supposed to occur under the influence of acids and of alkalies, in the yet more subtle chemical operations which are constantly occurring in the organs of living plants and animals, by which the arrangement of their components is modified and altered. In other cases, the obvious use of the saline matters is to furnish a skeleton or support for the plant. This is clearly the principal use of silica in the stem of the grass-tribe, and of oxalate of lime in many of the lichens.

It has already been remarked that the food of plants is derived from two sources, viz., the atmosphere and the soil. From the atmosphere, carbonic and nitric acids, ammonia and water are supplied; whilst from the soil are furnished the various saline materials necessary to the healthy growth of the plant. Now, in certain cases, all these materials, with the exception generally of carbonic acid and water, may be present in quantity too scanty to produce a luxuriant crop, and the great practical problem submitted to the farmer for solution is the discovery of the nature of the missing materials in any given case; and of the means by which these missing materials may be most cheaply and effectually supplied.

When a crop is carried off from the land, it necessarily takes with it a certain amount of mineral matters. If these mineral bodies be present in the soil in small quantity, and if fresh crops be continually carried off without provision for the return of the matters so removed, the land will in process of time become exhausted of one or more of these necessary ingredients, and sterility will be the inevitable result. One great object of the farmer in manuring his land is to restore these sparingly distributed but essential saline bodies in proportion as they are removed from the farm in the form of corn, of straw, of hay, or of stock which have been reared upon the produce of the land.

It is manifest that a fertile soil should retain its fertility if the manure supplied restore exactly those substances which previous crops had removed. There are few substances which more nearly fulfil this purpose than farm-yard manure; because the salts and mineral ingredients present in the food, pass off almost wholly into the excretions of the animal; and thus, the ingredients restored so far as the supply extends, are nearly identical with those which have been removed: since, if the ash obtained from a given weight of any specific crop be compared with the ash obtained by burning the excreta of animals fed upon an equal quantity of the same crop, the composition of the ash in the two cases will be nearly identical.

It is, however, well known, that the recent droppings of cattle are far more effectual as manure, than the ashes of such manure when burned; partly, because the recent manure contains carbon in a form which, during its decay within the soil, gradually supplies carbonic acid to the roots of the plant; but chiefly, as it appears, because it contains a large proportion of nitrogen, which, during its putrefaction, furnishes ammonia, or some other azotised compound, in a form suited to the wants of the growing crop.

It is owing to similar causes that night-soil and urine possess so high a value as manure. They are much richer in nitrogenized compounds, and in phosphates, than farm-yard manure; and indeed, they contain all the saline constituents of the corn and animal food, as well as almost all the nitrogen of the azotised constituents of the food which had been conveyed into the stomach, whether those azotised constituents had been assimilated or not. The Chinese have long been aware of the importance of these materials as manure, and they collect and carefully restore to their fields that which we in the pride of superior civilization discharge into sewers, and wastefully consign to the ocean, after allowing it to accumulate in offensive mud-banks within our tidal rivers, upon the shores of which, by the ebb and flow of the tide, it is alternately exposed to the heat of the sun and to the action of the water, under circumstances the most favourable to its decomposition, in consequence of which it is constantly contaminating the atmosphere of our large towns with its sickening effluvia.

(1453) *Varieties of Soil.*—In order to render the chemical action of manures intelligible, it will be necessary to take a rapid survey of the principal kinds of soil, and of the nature of the saline ingredients required by ordinary farm crops during their growth.

Soils vary greatly in physical characters, as well as in chemical composition. A soil may, for example, be described as *sandy*, *clayey*, *marly*, or *calcareous*, according as silica, alumina, or lime is the prevailing ingredient. The land will also be *porous* or *stiff*, *moist* or *dry*, partly owing to these peculiarities, and partly owing to its geological position; according as it rests upon sand, upon chalk, upon gravel, or upon clay; its character will also vary, partly owing to its site, according as it lies high or low, and as its surface is inclined or horizontal. But these considerations, though of high importance to the agriculturist, lie beyond the province of the chemist, whose principal attention must primarily be directed to the *chemical* peculiarities of the soil. In order that a soil be fertile it must not only be well drained and sufficiently watered, but it must possess a certain quantity both of organic and of saline ingredients.

Seeds, it is true, in some cases may be made to germinate and develope plants upon flannel, or in well-washed siliceous sand, if duly moistened from time to time with distilled water. The plants thus obtained may even sometimes flower; but they never produce fertile seed; and, if these plants be burned, the weight of the ash which they yield never exceeds that of the ash yielded by a quantity of seed equal to that from which the plants were raised. By adding suitable saline mixtures to washed siliceous sand, Wiegmann and Polstorf, however, obtained tobacco, oats, barley, and other plants in healthy growth, which furnished perfect seed. In these cases the plants had been supplied with those materials, the absence of which had in the previous experiments prevented their mature development. It must not, however, be hastily concluded from these results, that organic manures can advantageously be dispensed with in agriculture; experience has fully proved that a judicious combination both of organic and of saline manures is essential, and it is owing to ignorance of this fact that many of the patent mineral manures, when used alone, have so signally failed.

Different classes of plants, in order to the production of a luxuriant growth, require a soil possessed of physical qualities which must vary according to the kind of crop; and, in addition to this, each species of plant requires a variation in the chemical composition of the soil, suited to its peculiar habits. The prevailing and most abundant components of the soil, whether they be siliceous, aluminous, or calcareous, are not those which exert the greatest influence upon the development of the plant. They simply constitute the matrix in which the plant grows; and this matrix is more or less favourable to its growth, according as its physical character is more or less conformed to the wants of the plant; but the chemically active constituents of the soil consist of certain soluble saline compounds which are generally found in it in comparatively small quantities. In natural and fertile soils these salts are already present, either in an active or soluble form, or else in the passive or insoluble condition, stored up in rocks which have not as yet become disintegrated by exposure to the weather.

(1453 *bis*) *Liebig's Classification of Crops by their Ashes.*—In order to ascertain the nature of the salts which are essential to the

The results of such analyses suggest a probable reason why plants of different species do not all thrive equally well in a soil which may be highly productive for a particular crop; since a soil which abounds in the saline matters required by one crop, may be deficient in the ingredients necessary for the full development of plants of a different species. Root crops, and succulent plants generally, require abundance of alkaline and calcareous salts; and experience has shown that the green shoots of all plants are those which contain these constituents in the largest proportion; the grasses, and plants with stiff but not woody stems, are rich in silica; while the grain crops, and seeds in general, as well as those plants which are richest in azotised nutritive materials, abound in the phosphates of the alkalies and of the earths.

Not only does the composition of the ash vary in different plants, but its quantity varies also within wide limits. According to the estimate of Johnston, a ton of each of the following substances in its undried condition, contains upon the average the under-mentioned proportions of ash:—

One ton of	lb. of ash.	One ton of	lb. of ash.
Potato tops contains .	26	Wheat straw contains	220
Turnip tops ,,	48	Oat straw ,,	140
Hay contains from	90—180	Barley straw ,,	110
Pea haulm contains .	100	Rye straw ,,	60
Bean straw ,,	70	Rape dust ,,	120

It is evident that all plants must, to a certain extent, deprive the soil of its *saline* components; since no plant adds anything to these materials which already exist in the soil, but on the contrary, every crop that is carried off removes with it a corresponding amount of mineral material. Owing, however, to this important and undeniable fact, to which public attention was first strongly directed by Liebig, many persons have been tempted to overlook the necessity of organic materials in the manure; and considerable disappointment has often been experienced in finding that the restoration of mineral matters to the soil was not the only condition required to renew, or to preserve its fertility. Messrs. Lawes and Gilbert have rendered essential service to agriculture by their admirable researches upon this point, which have recalled public attention to a circumstance of cardinal importance to the agriculturist.

(1454) *Modes of Action of Manures.*—It would be a serious mistake to suppose that a supply of the proper manure can always

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It is now well known to the practical f
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the growth of the plant in the earliest s
its existence, and thus secures a far mor
when the supply of superphosphate is omi

The experiments of the same patient an
turist, which have been carried on in conjun
in a systematic manner, and upon a large
secutive years, have shown to the satisfac
observers that the direct supply of phosphates
quently does not materially increase the produc
wheat land already contains a far larger propo
distributed through it than is necessary to the gr
cessive crops of wheat. This circumstance appea
measure dependent upon a peculiarity in the mode
wheat plant; it strikes down the fibres of its roots
into the earth, by which means it is enabled to appro
phates of a much larger extent of soil than can come w
of the short tuft of fibres which constitutes the root of a

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[*] It is, however, probable that no manure acts simply as a s
that all such manures enter into the composition of the plant itself.
lating manures appear to supply through certain stages of the pla
a constituent or constituents, which, though present in the soil,
so in a sufficiently concentrated form, or which, owing to the im
velopment of the root, may not be sufficiently within the
at the particular time when they are most needed.

turnip.* It is also found, and apparently for similar reasons, that the addition of silicate of potash as a manure does not materially strengthen the stem in wheat, but that the employment of ammoniacal manures, including the best varieties of guano, enables large crops of wheat to be raised for several consecutive years on the same piece of land, the ammonia appearing to supply nitrogen to the gluten of the wheat, and acting also as a general stimulant to the growth of the plant. But although this has been established as a scientific fact, it is not recommended that this practice be substituted for the system of rotation at present in use; though it appears that with the aid of nitrogenous manures wheat may be grown in larger quantities, and more frequently in the rotation, without injury to the fertility of the soil.

It is a matter of experience that land which will not grow two remunerative crops of the same kind in succession (wheat for instance) without intermediate manuring, will yet, after a succession of turnips, barley, and clover, again be fit for wheat with comparatively light manuring; and that this system of rotation produces effects similar to those obtained by *fallowing*, or allowing the land to lie uncropped for a year. Lawes and Gilbert consider that clover and some other leguminous crops are especially valuable to the land, by supplying a quantity of nitrogenous organic matter to the soil, in a form particularly well calculated for assimilation by the succeeding wheat crop.

It is generally supposed that all the nitrogen found in combination in plants, has been obtained by the plant either from nitric acid or from ammonia, or from some azotised compound present in the soil in the form of manure; and that plants have not the power of directly assimilating nitrogen from the atmosphere. It appears probable however, that the leguminous plants generally introduced by the farmer in rotation, have a particular aptitude for condensing and retaining the nitrogen which is presented to them during their growth, and that they store it up; so that by the *debris* of its roots, and still more abundantly if ploughed into the land, a valuable source of nitrogen to succeeding crops. Wheat, on the contrary, accumulates but a comparatively small amount of nitrogen, and consequently thrives best when aided by the application of manures containing that element. Lawes and Gilbert, however, found that the addition of 5 lb. of ammonia per acre in the form of manure, produced an increase of about a bushel of wheat; from which it would appear, calculating from the known composition of the corn and the straw, that not more than about one-third of the quantity of nitrogen supplied in the manure is retained in the gluten of the seed, in the straw, and in other parts of the plant.

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* An interesting illustration of the influence of the development of the root upon the nature of the manure required, is afforded by a comparison of wheat and barley, which contain similar mineral constituents in nearly the same proportions:—wheat sown in autumn makes root all the winter, and is enabled to extract saline matters from the soil to a great depth; consequently it is seldom benefited by mineral manures directly applied, though it is greatly affected by the general mineral riches of the soil. Barley, on the other hand, is sown in spring; it throws out and depends upon root fibres nearer the surface, and is frequently much benefited by the use of manures containing phosphates.

Liebig accounts for the beneficial effects of the rotation of crops, by supposing that each plant in succession avails itself of saline matters which were unnecessary to the preceding crop. The process of fallowing appears to owe a certain portion of its efficacy to the gradual disintegration of the rocks, under the united influence of air, moisture, and alternations of temperature, in consequence of which, various substances, which were previously insoluble, are reduced to the soluble condition, and thus rendered available for the wants of the succeeding crop. It appears, however, probable, that the accumulation of compounds containing nitrogen within the soil during the period of fallow, has a material influence upon the following grain crop; but further experiments are still needed to elucidate the theory of fallowing.

The third mode in which manures act, viz. by the influence which they exert upon the components of the soil, is well exemplified in the application of lime, the most important uses of which are of an indirect character, although undoubtedly it is in some cases beneficial by supplying one of the mineral constituents essential to the healthy development of the plant.

Lime is applied to the land in the form either of slaked lime or of chalk. In the condition of slaked lime its chemical effects are exerted upon both the inorganic and the organic constituents of the soil. By its action upon the inorganic constituents, the insoluble silicates and the clays are decomposed: and potash, soda, alumina, and magnesia are set at liberty. Lime also decomposes salts of iron, rendering its oxide insoluble; it likewise partially decomposes common salt, forming carbonate of soda and chloride of calcium. The effects upon the organic constituents of the soil are even more important; for it is upon rich peaty soils which abound in organic matter, that the beneficial effects of lime are most evident. In such cases it occasions the decomposition of the organic matter, and gives rise to the formation of carbonic and nitric acids, as well as of ammonia; all of which bodies are important ingredients in the nutriment of the young plant; and at the same time the lime also liberates the saline constituents of a former vegetation, leaving them in a state well fitted for assimilation by the growing crop. This decay in the organic matter is produced by the simultaneous action of lime, atmospheric air, and moisture: it therefore takes place most rapidly near the surface, and is attended with the formation of nitric acid and ammonia, at the expense, in part, of the nitrogen of the atmosphere, just as occurs in the artificial nitre beds of Sweden, France, and other countries of the continent. Similar effects are produced, though much more slowly, by the action of chalk or carbonate of lime; and the beneficial results produced by the application of chalk are consequently less immediately perceived, and are diffused over a longer period of time.

In connexion with this indirect action of manures, it may be mentioned, that the beneficial effects of carbonic acid on the growth of plants are not limited to its direct action in supplying carbon to the crop; it performs a function not less important owing to its solvent power. The carbonates and phosphates of lime and of magnesia, and the oxide of iron are insoluble in pure water, but they are all dissolved to a small extent by water charged with carbonic acid, and are thus rendered available to the nutrition of the plant.

(1455) *Varieties of Manures.*—It has already been stated that the most important manures are those which are furnished by the excreta of animals; *guano* is one variety of this kind of manure; it consists of the decomposing excreta of sea-fowl which have fed upon fish; from its origin it abounds in phosphates and in ammoniacal salts; *farm-yard manure*, both solid and liquid, and night-soil and urine are also manures of a similar kind. Phosphates are abundantly supplied by *bone dust*, which also contains a considerable amount of gelatin. In burnt bones the gelatin is destroyed. The so-called *coprolites*, which consist principally of phosphate of lime, are probably debris of extinct animals, found in the tertiary beds of the Norfolk 'Crag,' and when reduced to powder and mixed with about half their weight of sulphuric acid, furnish one source of the manure which is known as *superphosphate of lime*. In this compound, the sulphuric acid liberates a portion of phosphoric acid, under the influence of which a portion of the bone earth is rendered soluble.

In the foregoing facts we see strikingly displayed the mutual de-referred to works on agricultural chemistry, particularly to Liebig's "Agricultural Chemistry," to Johnston's "Lectures on Agricultural Chemistry," and to the papers of Boussingault, in the *Annales de Chimie*, of Lawes and Gilbert, of Way, and of Voelcker, in the Journal of the Royal Agricultural Society.

§ II. NUTRITION OF ANIMALS.

(1456) *Chemical Nature of the Food of Animals.*—The food of animals is considerably less simple than that of plants. Even plants have no power of directly assimilating any elementary bodies with the exception of oxygen, though few compounds are less complicated in their constitution than water, carbonic acid, and ammonia. Animals, on the other hand, appear to require substances which have been elaborated by the organism of plants, and thus brought nearer to their own more complicated structure.

The best instance of an aliment fully capable of supporting life and expressly elaborated for that purpose, is furnished in the case of milk. Upon this the infant or young animal lives for some time exclusively, thrives, and grows rapidly; and as Prout has remarked, it contains four distinct principles, which may be taken as the types of the four chief varieties of alimentary substances. These types are, 1. the *aqueous*; 2. the *albuminous* or azotised, represented by casein; 3. the *saccharine*, supplied by sugar of milk, and 4. the *oleaginous*; to this ought to be added, 5. the *saline*, which is equally essential. It might, therefore, be anticipated that a suitable diet should contain a certain proportion of each of these principles; for, although the body possesses the power of altering and assimilating food to an extent varying greatly with the circumstances under which it is placed, yet experience has amply demonstrated that no one of these principles can be wholly withheld from any animal of the higher orders for a lengthened period without producing fatal results. It has been shown, for example, when animals are fed exclusively upon sugar, upon gelatin, or upon albumen, that they die of starvation; although when these different materials are given in mixture, the animal lives and thrives. It has also been observed that those aliments which are admitted to be the most nutritious, and which are most largely used as articles of food, are those which contain all these principles in due proportion. A good example of this kind is afforded in bread made from wheaten flour: its starch and sugar represent the saccharine principle, its gluten furnishes the azotised or albuminous material; water it of course contains; and it also tain these two principal modifications in the following proportions, the respiratory materials being all calculated, for the convenience of comparison, in the quantities of starch to which they would be equivalent:—

	Plastic Azotised Matter.	Respiratory Materials reckoned as Starch.	
Veal contains	10	1	
Hare's flesh	10	2	
Beef	10	17	
Horse beans	10	22	
Peas	10	23	
Fat mutton	10	27	= 11·23 fat
Fat pork	10	30	= 12·5 fat
Cow's milk	10	30	8·8 fat 10·4 sugar
Woman's milk	10	40	
Wheat flour	10	46	
Oatmeal	10	50	
Rye flour	10	57	
Barley	10	57	
Potatoes	10	86—115	
Rice	10	123	

Fat, sugar, starch, and alcohol must be regarded as articles which supply respiratory materials only; and when from external circumstances, such as exposure to cold, there is a greater demand upon the respiratory function, there is an instinctive craving for additional quantities of food which contain these substances, by which the temperature of the body is maintained above that of the surrounding air: thus the Laplander and the Greenlander drink train-oil, and are more prone to excess in spirits than the dweller in a more temperate climate. Alcohol, it must be observed, is not simply a respiratory food: it acts as a powerful stimulant upon the nervous system, and hence its effects are complicated. It is generally noticed that persons who are fond of pastry and sweetmeats, and consume them largely, have but little inclination for wine and alcoholic drinks, since the demand for respiratory material is supplied by the saccharine and amylaceous aliment taken; whereas, those persons who indulge largely in animal food have a greater craving for fermented drinks, which no doubt operate partially in supplying the deficiency in respiratory materials that such food exhibits.

The azotised ingredients of the food likewise evolve heat in the act of oxidation; but since these materials constitute the more highly elaborated, and less abundant, yet indispensable components of the food of animals, such a mode of consuming them must be considered as extremely wasteful; whilst at the same time these [illegible] are less perfectly adapted than true respiratory food, for the maintenance of animal heat.

From the table above quoted it appears that in milk and in the different varieties of corn, (which are the most perfect forms of nutritive matter,) the proportion which the plastic bear to the respiratory materials, are, 1 of the former, to from 3 to 6 of the latter. The proportions of these components, however, vary considerably in the food of different classes of animals, and their organs of digestion are modified to meet these differences. Thus the carnivora live on the flesh and blood of other animals, which in chemical and physiological properties are identical with their own, and which after digestion in the stomach are reduced to a soluble condition in this form they are absorbed, and enter into the composition o the animal. In the herbivora the organs of digestion are mor complicated, since their food contains only small quantities o nitrogen. It is found that animals require more or less food, i proportion as the compounds which contain nitrogen are less o more abundant in it. The nitrogen occurs in the food principall in the form of compounds which have the same composition a the albumen and fibrin of animals. Vegetable albumen and fibri are the principles which furnish plastic nutriment to the herbivora and if they be withheld for any protracted period, starvation ensues Hence it appears that one essential condition to the maintenanc of animal life is the assimilation of certain materials, which ar identical in constitution with the principal constituents of th blood. Animals do not possess the power of forming these principles, yet they produce a multitude of others from them by thei decomposition; for example, plants cannot produce the gelatinous principles, neither do they furnish the constituents of the brain both of which are elaborated in the animal frame from the components of the food. The azotised compounds, when taken alone are insufficient to support life; saccharine and oleaginous matter are absolutely necessary, and in the young, even of carnivora they form, in the shape of milk, a most important part of thei nutriment. Even the flesh diet of the carnivora contains a larg proportion of fat, which supplies the necessary respiratory material.

In our estimate of the importance of the different material which enter into the composition of food, we must not overlook the various salts; particularly common salt, phosphate of lime and the sulphates and phosphates of the alkalies. Common salt is essential for the supply of the hydrochloric acid of the gastric juice [illegible] the soda of the bile. Phosphate of lime is necessary to the building up of the bones; and not a cell or a fibre of the body can be formed without the presence of the soluble phosphates.

Liebig has pointed out the singular manner in which these different salts are associated in the different parts of the body; chloride of sodium, for instance, abounds in liquids which, like the blood and the serous exudations, have an alkaline reaction, and is commonly accompanied by tribasic phosphate of soda. Phosphate of potash on the other hand, occurs in liquids which, like the juice of the flesh, have an acid reaction.

(1458) *Process of Digestion.*—The preliminary cooking to which much of our food is submitted, is not essential to the process of digestion, but is generally resorted to in order to please the palate; but where a mixture of many kinds of food is to be assimilated by the stomach, the process of cooking may be made to assist the operations of digestion. The principal steps by which the food, after its reception into the mouth, is converted into a part of the living organism, are the following;—The food is first masticated and thoroughly mixed with the saliva. Animals which are carnivorous, chew their food less completely, and are supplied less abundantly with saliva, than those that are herbivorous. The reason is obvious, since in the carnivora, the fleshy nature of their aliments enables the latter to be more readily assimilated than is the case in the herbivora, many of which, by ruminating, subject their food a second time to a thorough trituration and intermixture with the saliva. Birds that are granivorous, are furnished with a strong hollow muscle, the gizzard, which is especially designed for the purpose of triturating the seed, to aid which, the birds swallow pebbles and gravel. The food, having been masticated and reduced to a pulp by intermixture with the saliva, is next transferred to the stomach, where it becomes mingled with the acid secretion of the gastric juice (1435). After remaining for a few hours in this organ, the principal proportion of the albuminous and fibrinous constituents of the food is brought into the liquid form; but the fatty matters remain unaffected, and the starchy components are but imperfectly converted into the soluble form of dextrin, or of sugar. From the stomach, the food now reduced to a pultaceous mass termed *chyme*, passes to the duodenum, or commencement of the intestinal canal, where it is mixed, first with the secretion from the liver, and then with that from the pancreas.

Physiologists are not agreed upon the share which the bile takes in the function of digestion, but both the bile and the pan-

creatic secretion are alkaline, and the chyme immediately af
admixture with these liquids, assumes the appearance of an em
sion; in its further passage along the intestinal canal, it is mi
with a secretion from the inner surface of the jejunum and of
ileum, which still further modifies the food, completing the conv
sion of starch into a soluble compound, and rendering the fa
matters capable of assimilation. In the small intestines a se
ration of the aliment into two portions is effected; the larger
these portions is absorbed into the system, the smaller porti
consisting of vegetable fibre and insoluble and undigested matte
becomes excrementitious, acquiring a peculiar odour, and is ul
mately rejected. The absorbed portion is taken up partially a
thin, milky liquid (the *chyle*) which is absorbed from the in
surface of the intestines by the lacteals, and these vessels emp
themselves through the thoracic duct, into the subclavian vein:
still larger portion is absorbed by the mesenteric veins, whi
transmit their contents to the liver, to be there further elaborat
before they are transferred by the hepatic veins to the rig
auricle of the heart.

One principal change wrought in the food, during its conversi
into chyme, consists in its being rendered soluble, and combin
with water; but it is evident that the mere fact of the conversi
of the food into the liquid form, is by no means the only essent
condition, since soluble matters, such as the casein of milk,
frequently first converted into a solid form in the stomach, and
then gradually redissolved; the elements of the food are thus
arranged, and if casein be the substance acted on, it is convert
into albumen; but the principal change is that described by Pr
as the *vitalizing* action of the stomach,—that change which fits de
organized matter for again becoming a portion of the living fra
The nature of this change is not at all understood. The solid fo
in which azotised matters are generally presented to the stoma
may be designed (by demanding a longer stay in this organ)
facilitate and allow time for the completion of this change; whi
the amylaceous and oleaginous principles of the food, which sim
supply the respiratory fuel, do not require so long a stay in t
stomach. It is worthy of remark that albumen, even after it h
been given as the sole constituent of the food, when it has on
been dissolved, cannot be detected as such in the fluid of t
stomach, either by boiling or by the action of nitric acid; it is n
till after it has passed through the duodenum, and becomes mix
with the secretions of the liver and the pancreas, that album
manifests itself by the ordinary reagents.

When digestion is duly performed, no gaseous products are set free; but when it is faulty, we often have a train of symptoms more or less distressing, owing to the evolution of carbonic acid, nitrogen, and hydrogen gases, which produce painful flatulence and distension. It may be to render this distension less liable to occur in infants, that milk contains an unfermentable variety of sugar.

There is a very great difference in the digestibility of the different articles used as food; some being completely chymified in two hours, and others requiring as much as six before this effect is produced. Very slight circumstances frequently interfere with the digestive process. Fats are apt to disagree, and so are all substances into the composition of which they enter largely; such as pastry, rich stews, and fried dishes; owing partly to the production of the peculiar volatile acids of fat during the processes of cooking or digestion, and partly owing to the difficulty with which such food is penetrated by the gastric juice. Where such food has been taken, the assimilating powers of the stomach are often interfered with, and the injurious effects thus occasioned are frequently manifested in the form of a sick-headache. Fermented liquors, if taken in small quantity, often afford a healthy stimulus to the stomach, but if taken in excess they arrest digestion and produce serious disturbance, independently of their enervating effects.

(1459) *Nutrition and Disintegration.*—Having traced the food into the blood, by the process termed by Prout *primary formative assimilation*, we may pass on to consider the course by which it becomes incorporated with the tissues of the living body. The offices of the blood may be considered under three principal heads:—1. that of *nutrition*, or reparation of the effete parts of the corporeal frame; 2. that of *respiration*, or the maintenance of animal heat; and 3. that of *secretion*.

1. *Nutrition.*—There is abundant evidence to show that the various tissues of the body are undergoing a constant succession of changes which are essential to the maintenance of life, and that the more actively the vital powers are exerted, the more rapidly do these various changes occur, necessitating the supply of food more frequently and abundantly. Shortly after the deposition of any particle has taken place in any particular tissue, it is in its turn removed to make room for a new and equally fleeting successor. This deposition of new matter is termed by Prout *secondary formative assimilation*, in opposition to the *secondary destructive assimilation*, by which the removal of the effete particles is effected. The principal organs of the body consist of albuminous and muscular tissue, with the exception of its solid frame-

work, and of those peculiar compounds which constitute the mass of the brain and of the nerves. Albumen and fibrin, the basis of these tissues, are contained ready formed in the blood, and they appear to be deposited at those points where they are needed, by a process somewhat analogous to that of simple coagulation. No advantage, however, would be gained, if the portions which they displace were to be re-absorbed in the form of albumen or of fibrin into the mass of the blood; for the deposited particles having once discharged their function in the system, cannot again be admitted to form integrant parts of it, until, as in the case of the albuminous and fibrinous portions of animals taken as food, they have been again subjected to the process of digestion, and have thus been fitted by the stomach for the performance of their various functions. The change which attends the absorption of matter once deposited is deep-seated, and is essentially connected with the manifestations of vital activity. No portion of albumen or of fibrin seems to be removed, as such, into the system; consequently the fibrin and albumen contained in the blood in a healthy state, must be considered as freshly elaborated, and as existing in it as a preliminary to its constituting an integral part of the body; and, therefore, as being in a form ready for assimilation. The effete tissues are decomposed at the moment of their removal, and are converted by the process of absorption into new and distinct compounds; thus furnishing the second source whence the blood derives its component parts, the process of absorption constituting the ***secondary destructive assimilation*** of Prout. This removal is usually effected by the agency of oxygen, supplied during respiration, and carried by the blood to every part of the system: the organic particles thus removed are therefore in a more oxidized form than that in which they were deposited, and they are absorbed at first into the blood itself, from which they are quickly eliminated in some of the excretions from it. Thus the nitrogen is removed partly in the form of urea, or of uric acid, and partly in that of ammonia. The carbon is chiefly got rid of as carbonic acid; and the phosphorus and sulphur, as phosphoric and sulphuric acids. These different matters are eliminated through four principal sources, viz. 1. the excreta of the alimentary canal; 2. the urine; 3. the cutaneous excretions; and 4. the pulmonary exhalation. Having already considered the principal chemical relation of the first three excrementitious products, we shall now confine our attention to the nature of the pulmonary exhalation.

(1460) 2. *Respiration.*—The important function discharged by the [illegible]sists in the admission of atmospheric air into the body, in such a manner as shall enable it to act upon and oxidize the blood; the most obvious chemical change which is produced in the respired air, consisting in the abstraction of oxygen from it, and the substitution of a bulk of carbonic acid nearly equal to that of the oxygen removed. The lungs act as an immense filter through which, in the higher classes of animals, the whole mass of the blood is made to circulate as often as it passes through the heart. The venous blood as it arrives in the lungs is of a deep purple colour. It leaves them of a florid arterial red. The general structure of the lungs is such that these organs may be regarded as consisting of two sets of tubes, the larger of which is for the admission of air. The air-tubes are subdivided into an infinite number of small ramifications, around which the blood-vessels are distributed in an extremely fine network; by this arrangement an immense surface is exposed to the air, with a comparatively small expenditure of space. The lining membrane of the air-tubes is kept continually moist by the secretion from their surface. Through this delicate membrane air passes readily by endosmosis into the blood-vessels beneath, and in consequence of this action the venous blood exchanges a portion of its carbonic acid with the oxygen held in solution by the liquid which bathes the surface of the air-tubes. The oxygen in this form obtains admission into the current of the circulation.* The mere displacement of carbonic acid from the blood, although unattended with any perceptible chemical change, produces an alteration of colour from purple to scarlet. During the circulation of the aerated blood through the minute capillary vessels of the body, the absorbed oxygen effects those chemical changes which are essential to the maintenance of animal life. The tissues are broken up; urea, carbonic, lactic, uric, sulphuric, phosphoric, and perhaps other times; and the numerous careful experiments published subsequently to those of Prout have fully established the correctness of these observations. It appears that the proportion of carbonic acid exhaled in a given time by the same animal, varies according to the rapidity of the circulation: the more vigorous the circulation, the larger is the quantity of carbonic acid evolved: thus, *cæteris paribus*, a larger quantity is formed after a meal than when the animal is fasting; the proportion is also higher when the animal is awake than when sleeping.

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* During the process of respiration a small quantity of nitrogen as well as of oxygen is absorbed, and this probably is one source of the nitrogen which is undoubtedly exhaled by the skin. It is probable that this nitrogen undergoes no chemical change, but is merely mechanically taken into the system owing to its solubility; the quantity in the air does not appear materially to vary, because if the blood be saturated with nitrogen, the amount of this gas which is separated will be equal to that which is evolved. By making animals respire in an atmosphere of oxygen and hydrogen, nitrogen is always found to be given out, since it is displaced from the blood by the hydrogen. According to the experiments of Regnault and Reiset (*Ann. de Chimie*, III. xxvi. 511.) warm-blooded animals, if made to respire in a confined space, always exhale an appreciable quantity of nitrogen; the amount, however, of this is so small as not to exceed $\frac{1}{100}$th part of the quantity of oxygen consumed. When the animals were in a state of exhaustion from want of food, an absorption of nitrogen commonly occurred to a similar extent. Traces of hydrogen, of carburetted hydrogen, and of ammonia are also present in respired air.

An important series of direct experiments upon respiration in man was undertaken by Scharling (Liebig's *Annal.*, xlv. 214, and lvii. 1). Other experiments upon the same subject by Andral and Gavarret will be found in the *Annales de Chimie*, III. viii. 129. Still more recently, Regnault and Reiset have published an extensive and elaborate series of researches upon the respiration of various classes of animals, from which several new and important conclusions have been deduced (*Ann. de Chimie*, III. xxvi.).

Scharling's experiments were performed upon persons of different ages who were placed in an air-tight chest, freely supplied with atmospheric air, which was deprived of carbonic acid by causing it to pass through a solution of potash. The respired air was transmitted through a succession of vessels, filled with sulphuric acid in order to retain moisture, with solution of potash to retain carbonic acid, and with sulphuric acid to retain moisture which the current of air might mechanically carry over from the solution of potash. The increase in weight of the last two vessels indicated the amount of carbonic acid. A continuous current of air through the apparatus was maintained by means of the regulated action of an air-pump, and the quantity of carbonic acid contained in the air of the chest at the close of the experiment was determined by direct analysis. By means of experiments conducted with this apparatus, it was ascertained that on an average, the production of carbonic acid during sleep amounted only to three-fourths of that given out by the same individual for an equal interval of time during the time that he was awake. It was also found that the production of carbonic acid was proportionately greater in children than in adults, as was to have been expected from the greater activity of the vital functions during the period of growth and development. The average production of carbonic acid was also greater in male than in female adults, as might be expected from the smaller size of the latter: but in adult individuals of both sexes, if of equal weight, *cæteris paribus*, the consumption of carbon appeared to be nearly equal. The same observer has also shown that the quantity of carbon exhaled in the form of carbonic acid from the surface of the skin, in the adult, does not on the average exceed one-third of an ounce in the twenty-four hours. In cold-blooded animals, however, the respiration effected through the skin is much more extensive; frogs and salamanders will continue to live for several days after the lungs have been removed, owing to this cutaneous respiration (Regnault).

The average quantity of carbon which passes off during the day from the lungs and skin of an adult man is estimated by Dumas at about 8½ ounces avoirdupois. These results have been almost exactly confirmed by the more recent experiments of Scharling. Andral and Gavarret found in their experiments (*Ann. de Chimie,* III. viii. 129) that the quantity of expired carbonic acid was nearly the same as that given by Scharling. Liebig's estimate is considerably higher; but it is probably less correct, since it was not founded on direct experiment, but was inferred from a rather loose estimation of the average amount of carbon contained in the rations allowed to a regiment of soldiers; making a somewhat arbitrary deduction for the amount of carbon eliminated in the urine and fæces.

It is, however, obvious that the amount of carbonic acid, and the proportion which it bears to the respired oxygen, must vary with the nature of the food. When carbon is converted into carbonic acid, the volume of this gas which is formed is exactly equal (under similar circumstances of temperature and pressure) to that of the oxygen which has entered into its composition; but when hydrogen is oxidized, the whole of the oxygen with which it has combined disappears from the gases exhaled; and a similar remark applies to that portion of oxygen which enters into combination, so as to form solid or liquid azotised compounds. It can therefore only happen that the proportion of carbonic acid expired, and of oxygen consumed shall be equal, when the whole of the inspired oxygen is employed in the oxidation of carbon. The direct experiments of Regnault and Reiset have, however, shown that this variation in the proportions of carbonic acid, and of respired oxygen, lies within very wide limits. From similar causes, when much fat is taken with the food a large portion of oxygen disappears. Thus it may be proved by calculation that when butter supplies the respiratory food, for every 31 volumes of oxygen absorbed, 21 only of carbonic acid can be produced; and a similar, but smaller, disappearance of oxygen occurs when alcoholic liquors have formed part of the food consumed. Regnault and Reiset found in their experiments that dogs when fed on meat, exhaled about 74 volumes of carbonic acid for 100 volumes of oxygen absorbed; but when fed on amylaceous substances the quantity of carbonic acid rose to 93 per cent. A dog which had been fed upon mutton suet, emitted only 69·4 per cent. of carbonic acid; the deficiency being in this case consumed in converting the excess of hydrogen in the fat into water. When animals which had been long kept without food were subjected to experiment, the percentage of carbonic acid was about the same as when they were confined to an animal diet; because the tissues of the animal constituted the source whence the carbonic acid was supplied; the animal was, in fact, feeding upon its own flesh. Rabbits fed upon vegetables emitted from 85 to 95 per cent. of carbonic acid, compared with the volume of oxygen absorbed; and granivorous birds yielded from 90 to 103 per cent., the volume of carbonic acid frequently exceeding that of the oxygen consumed. When these birds were confined to a flesh diet, the quantity of carbonic acid fell to about 67 per cent. of the oxygen consumed.

In the course of these experiments it was ascertained that, provided the quantity of oxygen be proportionately increased, an animal may continue to breathe without injury in an atmosphere containing a considerable amount of carbonic acid, the injurious effects of carbonic acid in the air appearing to depend rather upon the mechanical obstacle which it offers to the escape of the gas already in the blood, than to any directly poisonous action of the carbonic acid itself. By increasing the facility for its diffusion by the addition of oxygen, or even of hydrogen, to air already containing a considerable quantity of carbonic acid, the animals may continue to breathe such air without injury. Regnault found that the proportion borne by the carbonic acid exhaled, to that of oxygen consumed, is not altered when pure oxygen is substituted for atmospheric air, and the same relations were observed when the animals were caused to respire in an atmosphere consisting of a mixture of oxygen and hydrogen.

An interesting illustration of the great differences in the mode of respiration, which may occur even in the same animal under altered circumstances, is afforded by the observations upon hybernating animals. Marmots were found during their torpid condition to consume not more than one-thirtieth of the amount of oxygen which they required in their active state. These animals at the commencement of their hybernation are fat, but they lose weight considerably before they resume their active condition. A remarkable observation upon these animals was made by Sacc, and confirmed by Regnault and Reiset. The marmot whilst in a torpid condition increases in weight, owing to an absorption of oxygen which amounts to nearly one-half of that inhaled; this oxygen becomes converted into water, the greater portion of which is retained in the system for a while, but the animal at intervals evacuates it from the bladder, so that in the long run its weight becomes diminished. In fact, during its sleep its temperature is really maintained by the slow combustion of the store of fat which it had accumulated previous to its winter's repose.

The air which has passed through the lungs in the ordinary process of respiration, is by no means deprived of its oxygen; it usually contains about 4 per cent. only of carbonic acid; the greater portion of the air which is expelled during expiration has not proceeded further than the larger ramifications of the bronchi. In ordinary respiration 30 cubic inches, or about one-fifth of the quantity of the air in the lungs is changed with each act of respiration. The number of respirations in a healthy adult averages per minute from 18 to 20, but the bulk, as well as the frequency, of the inspiration varies with each individual, according to the circumstances in which he is placed, and the necessity of a larger or smaller supply of oxygen to the system.

If we assume that the average evolution of carbon by the lungs of an adult man amounts to 8·5 ounces of avoirdupois in twenty-four hours, it is easy to calculate the quantity of oxygen which is required during respiration for that period:—8·5 oz. of carbon would require about 22·66 oz., or 16·73 cubic feet of oxygen for its conversion into carbonic acid, and would yield 28,912 cub. in. of this gas at 60° F., barometer at 30 inches,—or 21 cubic inches per minute: consequently, if 10 lb. of blood pass through the lungs per minute, every pound of blood, in its passage through these organs must emit about 2 cubic inches of carbonic acid. Now, since for the oxidation of 8½ oz. of carbon, 22·66 oz. of oxygen are required, and since it is found that an adult emits on the average a volume of carbonic acid equal to 85 per cent. of the oxygen inhaled, it may be inferred (allowing 15 per cent. for the amount fixed of oxygen by hydrogen, &c.), that not less than 26·7 oz., or upwards of 1⅔ lb. of oxygen, are daily consumed by every adult; and allowing for 1·4 oz. of dry solid matter evacuated by the intestinal canal, and 2·2 oz. of solids by the urine, the whole of the remaining portion of the food (exclusive of about 4½ lb. of water, which is eliminated by the kidneys and the skin), must pass off in the gaseous form by the lungs.*

The exact form in which the compounds which are destined to produce animal heat exist in the blood is unknown, but there can be no doubt that the permanently alkaline condition of the blood (which Liebig attributes to tribasic phosphate of soda in the carnivora, and Lehmann to carbonate of soda in the herbivora) is concerned in a very important manner in this oxidating process; for it is uniformly observed that compounds of organic origin are much more readily oxidized in the presence of alkalies than they are when in a neutral or in an acid condition; doubtless because the products of oxidation being commonly acid, the presence of a base, with which those acids can combine, facilitates the formation of the acid, whether it be carbonic or any other acid compound.

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* The results obtained by Barral upon the average assimilation and consumption of food in twenty-four hours during summer and winter, conducted upon his own person, may here be cited (*Annales de Chimie*, III. xxv. 129).

Quantities in oz. avoirdupois of Food and Excreta in twenty-four hours.

Period of the Year.	Consumed.			Evolved.				
	Food taken.		Oxygen absorbed.	Water by skin and lungs.	Carbonic acid.	Total excreta.		
	Solid not dried.	Liquid.				Urine.	Fæces.	Nasal secretions.
						Not dried.		
In July . . .	24·4	59·7	27·42	40·27	31·34	36·14	2·66	1·19
In December .	39·2	57·9	37·44	45·43	43·32	39·97	5·00	1·15
Or in 100 parts								
In July . . .	75·4		24·6	36·1	28·8	34·7		0·4
In December .	72·2		27·8	33·8	32·3	33·2		0·7

Although these results are not free from objection, they possess considerable interest. The amounts of carbonic acid emitted, and of oxygen absorbed, are inferred from the difference between the quantity of carbon, hydrogen, and nitrogen, found by analysis in the food taken, and that furnished by the solid and liquid excretions. This mode of calculation necessarily involves these numbers in some uncertainty, since all the errors of experiment fall upon them. It was found that the total quantity of oxygen absorbed amounted to fully one-third of the entire weight of the solid and liquid constituents of the food. The proportion of nitrogen to that of carbon contained in the food taken was as 1 : 12·8. The excess of nitrogen in the food over that of the solid and liquid excretions varied from one-third to one-half; and this excess must have passed off through the skin and lungs; but this estimate is probably too high, although it does not attain to much more than 1 per cent. upon the volume of the carbonic acid. The proportion of nitrogen found in the solid excreta did not amount to one-fifth of that contained in the urine.

The proportion of carbonic acid exhaled in winter is much greater than in summer, and the quantity of water is also a little greater in winter. The latter circumstance may be explained by the fact, that more air passes through the lungs in winter than in summer, and it is less loaded with moisture on entering them; but in both cases the air quits them saturated with aqueous vapour at the temperature of the body, consequently it will carry off more moisture in the winter than in summer.

(1462) *Animal Heat.*—The temperature of the human body, whatever may be the temperature of the atmosphere, is uniformly maintained at 98° or 100°, that of birds at from 106° to 108°, and that of warm-blooded reptiles at about 85° F. But as the temperature of the air is many degrees, in this climate often 40° or more below that of the human body, it is clear, since the animal frame is subject to cooling at the same rate as other natural objects, that a constant supply of heat is necessary to the maintenance of this steady temperature. In order to diminish the quantity of heat required to be generated, animals are furnished with coats of hair, of feathers, of wool, and of other light, porous, non-conducting materials, which greatly retard their rate of cooling, and the thickness of which varies with the season of the year, and the average temperature to which the animal is exposed. Man supplies himself with clothing, which experience teaches him to adapt to the varying circumstances under which he is placed.

This constant evolution of heat in the living body is occasioned by the gradual combustion of the carbon and of the hydrogen supplied in the food; the combustion being effected by the agency of the respired oxygen. All bodies, when they enter into combination with others, whether quickly or slowly, evolve heat, and when the products resulting from combination are the same, the amount of heat which is developed for the same weight of the compound produced, is also identical (1478). Carbon and hydrogen are already combined with each other in the body, and, in the act of their combination have already evolved a certain amount of heat; the combustion of a hydro-carbon, therefore, will not produce the same amount of heat, as the combustion of an equal quantity of carbon and hydrogen not previously in a state of combination; still a very large quantity of heat will be developed during their oxidation, and if this oxidation be effected within the body, the heat thus liberated will necessarily contribute towards maintaining the temperature of the body. According to the experiments of Despretz, 1 ounce of pure carbon during combustion evolves heat enough to raise the temperature of 14,200 times its weight of water through 1° of F., or enough heat to convert into vapour 12·63 times its weight of water at 100°, or the temperature of the body; the heat developed by the combustion of 8·5 ounces of carbon should, therefore, suffice to evaporate 107·7 ounces of water daily, or, nearly 6·75 lb. This quantity of water is about double the average amount of that which is actually exhaled from the entire body in the twenty-four hours, the average being about 1 lb. from the lungs and 1½ lb. from the skin. The surplus heat from the carbon, as well as that from the hydrogen, the amount of which is not so easily estimated, is expended in keeping up the temperature of the body. Experiments have shown that animals exhale more carbonic acid in proportion to their weight, as their temperature is higher. It has been estimated that birds evolve half as much carbonic acid again, as the mammalia do; but Regnault finds that in some cases, the disproportion is much more considerable. The smaller the animal, the larger is the proportionate extent of its cooling surface, and consequently the larger is the quantity of carbon which must be oxidised within it in order to maintain a temperature equal to that of the larger animal; linnets, for instance, evolve 10 times as much carbonic acid in proportion to their weight, as the domestic fowl. Small animals consequently consume a much larger quantity of food in proportion to their weight than large animals, and this may account for the greater proportionate activity of many small animals when compared with larger ones.

Since the diffusion of animal heat over the different parts of the body is tolerably uniform, the source of heat should be diffused likewise. Provision appears to have been made for this essential condition, in the circumstance that the principal action of oxygen upon the constituents of the body, takes place in the capillary vessels which are distributed throughout the whole organized structure; and therefore, the heat resulting from this action is also equally distributed through the different parts of the body. A certain amount of chemical action doubtless takes place in the lungs, where the blood first comes into contact with the air, and this increased chemical action would be needed to supply the heat carried off by the vapour which passes off at each expiration; but the main oxidising actions occur deep in the structures of the body itself.

(1463) *Demand for Food varies with the temperature.*—Since then, the combustion of the hydro-carbonous portions of the blood are required for the due production of animal heat, it might be expected that, as the demand for heat varies at different seasons and in different climates, the quantity and the quality of the food demanded, should also vary accordingly. Experience proves that such is the case; the appetite is keener in winter than in summer, and the aliments which we are then in the habit of consuming partake more of a fatty and carbonaceous character: the inhabitants of the polar regions maintain the necessary supply of heat by an abundant consumption of blubber and train-oil, while those who live in tropical climates content themselves with a lighter and more succulent vegetable diet. It is remarked by Liebig that the habits of life formed by the European are in some degree retained when he makes his abode under the burning sun of an Indian sky. Under such altered circumstances he still stimulates his appetite to consume the flesh diet to which he has been accustomed, and diseases of the liver are the consequence. This gland secretes a fluid rich in carbon, and in certain cases may act as one outlet of hydrocarbonous matters to the system. Respiration in a hot climate takes place with diminished frequency. It must also be remembered, that equal volumes of air admitted to the lungs by respiration at high, and at low temperatures, contain very different weights of oxygen; air at 40° containing one-tenth more by weight of oxygen than an equal bulk of air at 90°. Less carbon, therefore, is thrown off by the lungs in equal intervals of time, in a hot climate than in a cold one, by which means the too rapid production of animal heat is avoided; but the excess of carbon carried into the system must, nevertheless, be got rid of, and this must be effected in a manner that shall not produce heat. Owing to the beautiful compensating system upon which our bodies are constructed, one organ, if necessary, can relieve another from its burden, and the liver carries off this excess of carbon in an unburned form; provided the quantity be only moderate, this vicarious action may be effected without inconvenience, but if it be excessive, enlargement and congestion of the gland ensue, and disease, more or less serious, is the result. In a dry state of the atmosphere, however, less duty falls upon the liver, inasmuch as free evaporation goes on from the surface both of the lungs and of the skin, and thus the temperature of the body is reduced. In dry weather, therefore, carbon may be emitted by the lungs in larger quantity without inconvenience; but when the temperature of the air is high, and at the same time loaded with moisture, this source of relief is cut off, and an oppressive sensation of languor is experienced.

There is still a great want of accurate direct experiments on the production of carbonic acid under great differences of temperature, and a correct series of experiments on this subject, in arctic and in tropical regions, would be highly valuable both to the physician and the physiologist.

On the whole, then, it appears that the saccharine and oleaginous portions of our food are those which are best adapted to the maintenance of respiration and of animal heat: when, however, these materials are given in excess, they are thrown off by the liver and the kidneys: Tiedemann and Gmelin found, when they fed animals on butter and starch, that the urine was loaded with fatty matter, and bilious diarrhœa was an almost constant attendant. The azotised principles of the food are necessary for the reproduction of the muscular and other tissues, and go to form the azotised principles of the blood; and hence the importance of a mixed diet for the due support of the vital functions. The nutritive value of different articles of food is, therefore, entirely relative, and is dependent upon the proportion in which each is mingled with other bodies, in which the four staminal principles are combined together in due proportion.

It must not be overlooked, however, that the most advantageous mixture of nutritive materials will vary with the circumstances under which the animal is placed. In the human species, the milk is adapted to the wants of the new-born infant, which will be wrapped in clothes, and shielded from the weather, and the materials consist of about 10 parts of plastic matter, 10 of fat, 20 of sugar, and 0·6 of salts. In the case of the cow, where the young animal is more exposed to the vicissitudes of the weather, the proportion of these constituents is altered, the milk containing to every 10 parts of plastic material, 11·11 of fat, and 14 of sugar. The composition of the milk at different periods of lactation also varies in an important manner, in order to meet the altering wants of the young animal in the successive stages of its growth.

A few animals are entirely carnivorous ; but it must be remembered that all flesh, even that which is usually considered to be lean, contains, in addition to azotised matter, a certain quantity of the oleaginous or fatty principle which is needed for the support of respiration. The herbivora consume with their food, large quantities of saccharine and amylaceous compounds, which, by the abstraction of oxygen, are converted into fat ; such animals are capable of being fattened in a remarkable manner, whereas the carnivora seldom acquire any great store of fat, in consequence of a deficient supply of the material best adapted for conversion into that substance.

It has been already remarked, that when increased demands are made upon the strength of animals, as in taking exercise, the number of respirations is increased, and the circulation quickened, more oxygen is absorbed, and more carbonic acid evolved ; and it appears probable that this increased demand upon the muscular effort, is for the time, supported by the increased stimulus resulting from the more rapid chemical action upon the tissues of the body. For a full consideration of the subject of animal heat, the reader is referred to Liebig's treatise on *Chemistry in its Application to Physiology and Pathology.*

(1464) 3. *Secretion.*—Having now considered the functions of the blood in regard to nutrition, and to respiration, we have lastly to offer a few remarks upon the process of secretion. It is worthy of remark that in every instance where a purely excrementitial product is formed, the substances excreted are produced in the mass of the blood, at a distance from the point at which they are separated. The bile furnishes an exception, but, as it has been already stated, the greater portion of this fluid is re-absorbed into the system; it therefore cannot be considered as purely excrementitious. In experiments in which the kidneys have been removed from animals, uric, phosphoric, and sulphuric acids, as well as urea, are found to accumulate in the blood; the kidney is, therefore, not to be looked upon as an oxidizing or acidifying organ, but as an organ through the agency of which acids are separated from the system, combined with, and nearly neutralized by, alkaline matters. A similar principle holds good in the case of the lungs, which may be viewed as a gland by which carbonic acid is excreted; the carbonic acid, however, not being formed by the lungs, but simply eliminated by their action. It appears, therefore, that those organs which are destined for the separation of excretions from the body do not form the various substances, but simply eliminate them. The case, however, is otherwise with the glands which furnish substances destined to be consumed subsequently by the economy: these glands in such cases seem to effect a true transformation of the blood, one part of which forms the peculiar matter of the secretion, (as for example, sugar of milk in the mammary gland,) the other, or complementary portion, is returned into the mass of circulating fluid. The true mechanism of secretion is at present unknown. It has been imagined that secretion may present a certain analogy with the case of vinous fermentation, in which, little as we know of the cause, we understand the conditions requisite to produce it; for it appears that the main point consists in the presence of certain organic molecules, since it is found by the experiment of placing yeast in a tube closed with filtering paper, and dipping into a solution of syrup (page 105), that actual contact with those molecules is necessary to produce the decomposition, the liquid in the tube being the only part which ferments: hence we may conceive why blood out of the gland undergoes not the same changes as when circulating through it. No satisfactory attempt has hitherto been made to explain why one substance should produce one kind of decomposition, and a different substance a totally different decomposition, although the compound operated on be the same in both cases.

CHAPTER XIV.

§ I. ATOMIC VOLUMES. § II. ATOMIC HEAT. § III. HEAT OF COMBINATION.

(1465) HAVING now completed our survey of the different classes of organic compounds, we may proceed in the last place to review briefly some points connected with the theory of the atomic constitution of matter which could not conveniently be discussed until the chemical properties of the various compounds, both organic and inorganic, had been described.

Two theories of the composition of material bodies have been maintained with varying degrees of credit from the earliest ages of the Grecian philosophy to the present time; the one founded on metaphysical; the other, and now the generally received opinion, based on physical considerations.

Upon the first view of the constitution of matter, it is supposed that the particles of which bodies consist, are capable of subdivision without limit. Every particle of matter must possess an upper and a lower surface, and therefore it is conceivable that these surfaces may be separated from each other.

The second view, which was upheld, amongst other illustrious men, by Sir Isaac Newton, maintains that though matter is susceptible of subdivision into molecules of inconceivable minuteness, there is a point beyond which no power within the reach of man, whether mechanical or chemical, can carry this reduction, and these particles are hence appropriately termed *atoms* (or indivisibles). This view has acquired great additional probability since the phenomena of chemical combination have been better understood and more accurately examined. Upon this *atomic* hypothesis, as now generally admitted, it is supposed that the particles of which each element consists, have a definite and uniform magnitude.

The phenomena of chemical combination, and the laws of definite, multiple, and equivalent proportion, indeed admit of a simple explanation by the aid of this hypothesis, which, as developed by Dalton, has received the name of the *atomic theory*.

Dalton assumes that the ultimate particles of any given element are of uniform magnitude, and possess the same relative weight; but that the particles of different elements differ from each other in weight, and possibly also in magnitude. When chemical combination takes place between any two elementary bodies, combination is supposed to occur between them atom to atom. Hence the proportions in which bodies unite must of necessity be definite and invariable. In like manner the law of multiple proportion becomes a physical necessity, since compounds must be formed by the union of 1 atom of one of the elements with 1, 2, 3, 4, or more atoms of the other element; or 2 atoms of one element with 1, 3, 5, or 7 atoms of the other.

The equivalent numbers of the different elements simply express the relative weights of their atoms, and hence the term *atomic weight* is by many writers used as synonymous with that of *chemical equivalent* (13), or *combining proportion.*

Nothing is known of the absolute size or weight of these ultimate particles of matter, but it appears to be certain that the amount of heat, of electricity, and of other forces associated with each chemical atom, is perfectly definite. We are also in ignorance of the form of these atoms, for it is clearly proved that the minutest particle of matter which the eye, assisted by the most powerful microscope, is able to perceive, yet consists of an indefinite multitude of atoms: the configuration of such minute visible particles cannot therefore furnish any clue to the shape of the ultimate particles of which the body is composed. It is, however, not improbable that the atoms of the elementary bodies are either spherical or spheroidal; the simplicity of such forms being most in harmony with the equality of attraction in different directions.

§ I. Atomic Volumes.

(1466) Various attempts have been made to determine the relative sizes of the atoms of different elements, some of which will be briefly noticed almost immediately. It is probable that, even in solids, the distances between their component particles are much greater than the diameters of the particles themselves; and in gaseous bodies these intervals of course will be very much greater than in liquids or in solids. The observations of Dalton and of Gay Lussac upon the effects of temperature upon gases led these philosophers to the conclusion that the expansion and contraction which aeriform bodies undergo when subjected to equal increments or decrements of temperature, *ceteris paribus*, is uniform; and it has hence been argued, from the results obtained by Gay Lussac, and by Dalton, that in aeriform substances the relative distances between the component particles of all gases must be uniform in all. More accurate researches have, however, shown that, although for general purposes the law of the uniformity of expansion of gases by heat may be admitted, yet it is not absolutely true, and that the departure from this law is particularly evident in the case of those vapours and gases which are readily liquefied by pressure (*note*, p. 169, Part 1.). Experiment has proved, that in the case of elementary bodies which in the gaseous form, the equivalent quantities of these bodies are portionate to their densities, as shown in the table given below, d the equivalents of these elements are consequently represented numbers which exhibit the ratio of their atomic weights.

Oxygen, phosphorus, and sulphur form exceptions to this rule. erhardt, however, induced by other considerations, doubles the usual uivalent of oxygen, in favour of which procedure he has shown at strong arguments may be adduced. If his view be adopted, the nomaly disappears in the case of oxygen, and some of the other xceptions may be explained, by admitting that in such instances the epulsive power of heat may be insufficient to cause the complete esolution of a body into its ultimate atoms; that in phosphorus, nd in arsenic, for example, two of these atoms may remain associated together, whilst in the case of sulphur not less than six atoms may be so associated; inasmuch as instances occasionally occur, as in the case of copper and mercury, in which two atoms of a substance combine as one, so that such a supposition is not in contradiction to known analogies. At a temperature below 1500° an equivalent of sulphur yields a volume of vapour equal only to one-third of that of one equivalent of oxygen at the same temperature; but if heated beyond 1800° it becomes dilated, till it occupies the same bulk as an equivalent of oxygen similarly heated. This alteration in the equivalent volume, which sulphur experiences at very high temperatures, is strongly in favour of such a view as that just given.

In compound gases it might be supposed that the increased bulk occupied by the compound atom would interfere with the regularity of their expansion, but the bulk of solid matter in any gas is so small compared with the entire space which it occupies, that no sensible irregularity due to this cause is perceivable.

Specific Gravity and Combining Volume of the Elementary Gases.

1 eqt. in grains of the undermentioned elements yields in Cub. In. Grs.		Cb. In.	Comb. vol.	Specific Gravity. Calculated.	Observed.	Name of Observer.
8	Oxygen .	23·33	1		1·10563	Regnault
31	Phosphorus	23·33	1	4·284	4·4200	Dumas
75	Arsenic .	23·33	1	10·1670	10·6000	Mitscherlich
16	Sulphur .	7·77	⅓	6·6337	6·617	Dumas
1	Hydrogen .	46·66	2	0·0691	0·0692	Regnault
14	Nitrogen .	46·66	2	0·9674	0·9713	Regnault
35·5	Chlorine .	46·66	2	2·4531	2·47	Gay Lussac
80	Bromine .	46·66	2	5·5281	5·54	Mitscherlich
127	Iodine . .	46·66	2	8·756	8·716	Dumas
100	Mercury .	46·66	2	6·9101	6·976	Dumas

The third column of this table indicates the bulk of vapour

Table showing the Density of several Compound Gases and Vapours.

[*Continued.*]

Name.	Constituents.		Formulæ.	Density.		Authority.
				Calculated. H = 1.	Observed. Air = 1.	
	vols.	vols.				
Hydrocyanic acid . . .	2 H	2 Cy	$\frac{HCy}{4}$	14	0·9476	Gay Lussac
Deutoxide of nitrogen .	2 N	2 O	$\frac{NO_2}{4}$	15	1·0389	Bérard
Muriate of Ammonia .	4 H_3N	4 HCl	$\frac{H_4NCl}{8}$	13·4	0·89	Bineau
Hydriodate of phosphuretted hydrogen . .	4 H_3P	4 HI	$\frac{H_4PI}{8}$	40·5	2·77	ditto
Hydrobromate do. .	4 H_3P	4HBr	$\frac{H_4PBr}{8}$	28·7	1·906	ditto
	3 *Volumes condensed into* 2.					
Steam . . .	2 H	1 O	$\frac{HO}{2}$	9	0·6235	Gay Lussac
Protoxide of nitrogen .	2 N	1 O	$\frac{NO}{2}$	22	1·5200	Colin
Hypochlorous acid .	2 Cl	1 O	$\frac{ClO}{2}$	43·5	2·9	Calculated
Peroxide of chlorine .	2 Cl	4 O	$\frac{ClO_4}{4}$	33·8	2·322	Gay Lussac
Peroxide of nitrogen .	2 N	4 O	$\frac{NO_4}{4}$	23	1·720	Mitscherlich
Calomel . .	4 Hg	2 Cl	$\frac{Hg_2Cl}{4}$	117·7	8·350	ditto
Dibromide of mercury .	4 Hg	2 Br	$\frac{Hg_2Br}{4}$	140	10·140	ditto
*Carbonic oxide	2 C?	1 O	$\frac{CO}{2}$	14	0·967	Wrede
†Sulphuretted hydrogen .	2 H	1 S?	$\frac{HS}{2}$	17	1·1912	Gay Lussac
Seleniuretted hydrogen .	2 H	1 Se?	$\frac{HSe}{2}$	40·6	2·795	Bineau
Telluretted hydrogen .	2 H	1 Te?	$\frac{HTe}{2}$	65	4·489	Calculated
Sulphurous acid	1 S?	2 O	$\frac{SO_2}{2}$	32	2·247	Berzelius
Selenious acid	1 Se?	2 O	$\frac{SeO_2}{2}$	55·6	4·03	Mitscherlich
Carbonic acid	2 CO	1 O	$\frac{CO_2}{2}$	22	1·529	Regnault
Sulphuric acid	2 SO_2	1 O	$\frac{SO_3}{2}$	40	3·01	Mitscherlich

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* Here it is assumed that 1 equivalent of carbon yields 2 volumes of vapour.

† Sulphur, in accordance with Bineau's researches upon it at high temperatures, is assumed to have an equivalent volume equal to that of oxygen; and selenium and tellurium are supposed to be analogous to it.

Table showing the Density of several Compound Gases and Vapours.

[*Continued.*]

4 *Volumes condensed into* 2.

Name.	Constituents.		Formulæ.	Density.		Authority.
	vols.	vols.		Calculated. H = 1.	Observed. Air = 1.	
Corrosive sublimate .	2 Hg	2 Cl	$\frac{HgCl}{2}$	135·5	9·800	Mitscherlich
Bromide of mercury .	2 Hg	2 Br	$\frac{HgBr}{2}$	180	12·160	ditto
Red iodide of mercury .	2 Hg	2 I	$\frac{HgI}{2}$	227	15·600	ditto
Chlorocarbonic acid .	2 CO	2 Cl	$\frac{COCl}{2}$	49·5	3·6808	J. Davy
Ammonia . .	6 H	2 N	$\frac{H_3N}{4}$	8·5	0·590	H. Davy
Bisulphide of carbon . .	2 S ?	2 C	$\frac{CS_2}{2}$	40	2·6447	Gay Lussac
Chlorosulphuric acid	2 SO$_2$	2 Cl	$\frac{SO_2Cl}{2}$	67·5	4·703	Regnault
Dutch liquid .	4 Cl	4 CH	$\frac{C_4H_3Cl,HCl}{4}$	49·5	3·478	ditto
Monochlorinated do.			$\frac{C_4H_2Cl_2,HCl}{4}$	66·7	4·613	ditto
Bichlorinated do. . .			$\frac{C_4HCl_3,HCl}{4}$	84·0	5·767	ditto
Trichlorinated do.			$\frac{C_4Cl_4,HCl}{4}$	101·25		
Sesquichloride of carbon			$\frac{C_4Cl_4,Cl_2}{4}$	118·5	8·157	ditto
Dichloride of sulphur .	2 S ?	2 Cl	$\frac{S_2Cl}{2}$	67	4·70	Dumas
Fluoride of boron . .	2 B ?	6 Fl ?	$\frac{BFl_3}{4}$	34·9	2·312	ditto
Terchloride of antimony	2 Sb ?	6 Cl	$\frac{SbCl_3}{4}$	117·7	7·8	Mitscherlich
Terchloride of bismuth .	2 Bi ?	6 Cl	$\frac{BiCl_3}{4}$	159·2	11·16	Jacquelain
5 *Volumes condensed into* 2.						
Sesquichloride of carbon (liquid)	4 C	6 Cl	$\frac{C_2Cl_3}{2}$	59·25	4·082	Regnault
6 *Volumes condensed into* 2.						
Cyanogen . .	4 C ?	2 N	$\frac{C_2N}{2}$	26	1·8064	Gay Lussac
Bichloride of carbon . .	4 C ?	8 Cl	$\frac{C_2Cl_4}{4}$	77	5·3	Regnault
Marsh gas . .	4 C ?	8 H	$\frac{C_2H_4}{4}$	8	0·557	Thomson
Bichloride of titanium .	2 Ti ?	4 Cl	$\frac{TiCl_2}{2}$	95	6·836	Dumas

Table showing the Density of several Compound Gases and Vapours.

[*Continued.*]

Name.	Constituents.		Formulæ.	Density.		Authority.
				Calculated. H = 1	Observed. Air = 1.	
Bichloride of tin* . . .	vols. 2 Sn ?	vols. 4 Cl	$\frac{SnCl_2}{2}$	129·8	9·199	ditto
Fluoride of silicon . .	2 Si ?	4 Fl ?	$\frac{SiFl_2}{2}$.	52·2	3·600	ditto
Chloride of silicon . .	2 Si ?	4 Cl	$\frac{SiCl_2}{2}$	85·2	5·939	ditto
Chlorochromic acid .	2 Cr ?	2 O,2 Cl	$\frac{CrO_2Cl}{2}$	77·8	5·52	ditto

Some remarkable irregularities have been observed in the volume occupied by the vapours of many volatile compounds. Many of these vapours at a low temperature have a density much greater than that which they possess when more strongly heated. The vapours of the volatile acids, such as the formic and the acetic acids in particular, exhibit this anomaly in a marked degree (1153).

(1468) *Atomic Volumes of Solids.*—1. *Simple Bodies.*—It has been supposed that if the atoms of all the elementary bodies were of the same size, the specific gravities of these bodies in their solid form would be in the same proportion as their chemical equivalents. In such a case, however, either the particles composing the solid must be in actual contact, or the intervals between the particles must be equal. Dumas showed many years ago that the specific gravity of certain isomorphous metals was nearly in the direct ratio of their atomic weights. Since then Schröder and Kopp have pointed out a number of remarkable relations between the densities of different bodies and their chemical equivalents. Kopp has shown that many of the elementary bodies may be arranged in groups, each group consisting of members in which the atomic volume is identical. If such weights of the different elementary bodies as represent the chemical equivalents of each be compared together, the bulk occupied by each body will be such as is indicated in the column headed *atomic volume* in the following table:—

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* The vapour volume of one equivalent of each of the different metals is assumed to correspond with that of an equivalent of hydrogen, and consequently to be double that of an equivalent of oxygen, and the same assumption is made in the case of silicon and of boron.

Table of the Atomic Volumes of Elementary Bodies.

Names of Elements.	Equiv. Number O=100.	Atomic Vol.	Calculated Density*	Observed Specific Gravity.
Carbon	75	22	3·41	3·55, 3·336, Jacquelain
Cobalt	369	44	8·39	8·49, Brunner; 8·51, Berzelius; 8·95, Rammelsberg
Copper	395	44	9·00	8·96, Berzelius; 8·72, Karsten; 8·92, Marchand and Scherer
Glucinum	87·5	44	1·99	2·1, Debray
Iron	350	44	7·95	7·84, Broling; 7·79, Karsten
Manganese	345	44	7·86	8·03, Bachmann; 8·01, John
Nickel	369	44	8·39	8·40, Tourte; 8·82, Tupputi; 8·60, Brunner
Iridium	1232	57	21·6	?
Osmium	1244	57	21·8	?
Palladium	666	57	11·7	11·3—11·8, Wollaston
Platinum	1232	57	21·6	21·0, Borda; 21·5, Berzelius, Wollaston
Rhodium	651	57	11·4	11·0, Wollaston; 11·2, Cloud
Zinc	406	57	7·14	7·14, Wertheim; 6·86—7·21, Berzelius
Aluminum	171	66	2·59	2·56—2·67, Deville
Chromium	328	66	5·00	5·09, Thomson
Molybdenum	575	66	8·63	8·62—8·64, Bucholz
Tungsten	1150	66	17·4	17·2, Allen; 17·4, Bucholz; 17·6, D'Elhuyart
Cadmium	697	81	8·60	8·60, Stromeyer; 8·63, Karsten, Kopp
Magnesium	150	86	1·743	1·743, Bunsen
Mercury	1250	91	13·6	13·6, Kupffer, Karsten; 13·56, Faraday
Selenium	495	103	4·8	4·8, Schaffgotsch; 4·30—4·32, Berzelius
Sulphur	200	101	1·99	1·99—2·05, Karsten; 1·99, Breithaupt
Tin	735	101	7·28	7·28, Herapath; 7·29, Kupffer, Karsten
Arsenic	600	105	5·7	5·7—5·96, Guibourt; 5·67, Herapath
Lead	1294	114	11·35	11·44, Berzelius; 11·35, Herapath; 11·33, Kupffer
Gold	2458	128	19·2	19·34, G. Rose; 19·26, Brisson
Silver	1350	128	10·53	10·53, G. Rose; 10·4, Karsten
Tellurium	800	128	6·25	6·25, Berzelius
Lithium	81	136	0·593	0·593, Bunsen
Calcium	250	158	1·578	1·578, Bunsen
Phosphorus	387	211	1·83	1·83, Schrötter; 1·77, Berzelius
Strontium	550	216	2·54	2·54, Bunsen
Antimony	1503	224	6·7	6·71, Marchand & Scherer; 6·7, Karster
Bismuth	2660	270	9·84	9·88, Thenard; 9·83, Herapath; 9·8 Marchand and Scherer
Bromine	1000	320	3·12	(liquid) 2·99, Löwig; 2·97, Balard
Chlorine	443	320	1·38	(liquid) (1·33 about), Faraday
Iodine	1587	320	4·95	4·95, Gay Lussac
Sodium	287	295	0·972	0·972, Gay Lussac and Thenard
Potassium	487	562	0·865	0·865, Gay Lussac and Thenard

The atomic volume (or specific volume) of any substance, simpl or compound, may be calculated by dividing its chemical equivalen its specific gravity. Thus, if d=the density or specific gravity, q, the chemical equivalent, and v = the atomic volume, $\frac{q}{d} = v$.

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* In the above table, the column headed *calculated density* indicates th numbers which, if used as divisors of the equivalent numbers, yield the nun bers which are adopted as the *atomic volume* of the body.

A simple mode of determining experimentally the atomic lume of a body was employed by Playfair and Joule. Their paratus or *volumenometer* consists of a globular flask provided th a long narrow neck, about twelve inches in length, graduated om below upwards, to indicate grains of water. The flask is rovided with a tubulure (accurately fitted with a ground stopper) r the admission of the solid body for experiment. When the strument is to be used it is to be filled up to the mark 0° on the tem, with water, with oil of turpentine, or with some liquid which exerts no solvent action on the body. It is then inclined o one side, the stopper removed, and a weighed quantity of the solid for experiment, is carefully introduced: the stopper is then replaced, and the number of divisions which the liquid is raised in the stem indicates in grains the quantity of water which has been displaced. Thus, if 350 grains of iron (an equivalent in grains) be introduced, the liquid will rise 44 divisions in the stem of the instrument, indicating the equivalent volume by simple inspection. If the quantity of the substance employed be less, say one-third, or one-fourth of an equivalent in grains, the rise in the stem, when multiplied by 3 or by 4, as the case may be, indicates the atomic volume of the body under experiment. The same experiment also furnishes the data for determining approximatively the specific gravity of the body, since the weight of the substance used, when divided by the number of divisions which the liquid has risen (corresponding to the weight of the bulk of water equal to the solid) will, of course, give the specific gravity.

Schröder, Kopp, and most of the chemists who have worked upon this subject, have made their calculations upon the oxygen scale of equivalents which has been adopted in the table.

From the foregoing table, it is apparent that several groups of *isometric* elementary bodies (that is to say, bodies possessed of equal atomic volume), exist; and that between other groups, multiple relations of a simple kind occur, thus:—

1. The atomic volume of the group containing cobalt, copper, glucinum, iron, manganese, and nickel, is double that of carbon.

2. There is some uncertainty about the true atomic volume of iridium and osmium, since their specific gravities are not accurately known, but from the isomorphous relations of these bodies they are classed with platinum.

volumes. The following table contains the specific gravity and atomic volume of a few dimorphous substances.

Dimorphous bodies.	Specific Gravity.	Atomic Volume.
Diamond	3·41	22
Graphite	2·09	36
Native Sulphur (Octohedral)	2·05	97·5
Prismatic Sulphur . . .	1·98	101
Viscous Sulphur	1·957	102
Iceland Spar	2·72	229
Aragonite	3·00	211

(1470) *Disturbing influence of Temperature.*—There can be no doubt that the atomic volume of a body is a character as definite as is its specific gravity, or its equivalent number; but the determination of its precise amount is opposed by some peculiar and considerable obstacles. One of these arises from the difficulty of accurately determining the specific gravity of a solid, under circumstances which shall be properly comparable. Since the bulk of all bodies varies with the temperature, and increases as the temperature rises, the specific gravity, as taken in the ordinary method, will be liable to variation according to the temperature. This would be of little consequence, however, if the amounts of expansion produced by equal increments of heat were alike in all bodies; but experiment distinctly proves that this is not the case, and the great extent of this variation amongst many of the simple bodies, may be seen by the subjoined table:—

Cubic Expansion of some of the Metals from 32° to 212°.

Metal.	Equal Bulks.		Atomic Volumes.		Approximative Ratio of Expansion for at. vols.		Authority.
	parts at 32°,	gain at 212°,	parts at 32°,	gain at 212°,			
Iron . .	100	0·354	44	0·147	1	0·150	Dulong and Petit.
Platinum	100	0·264	57	0·150			
Copper .	100	0·515	44	0·226	1·5	0·225	Lavoisier and Laplace
Zinc . .	100	0·882	57	0·332	2	0·300	Smeaton.
Gold . .	100	0·440	128	0·582	4	0·600	Lavoisier and Laplace
Tin . .	100	0·581	101	0·586			Do
Antimony	100	0·325	224	0·728	5	0·750	Smeaton.
Silver . .	100	0·573	128	0·733			Lavoisier and Laplace
Lead . .	100	0·854	114	0·974	6·5	0·975	Do
Bismuth .	100	0·417	270	1·126	7·5	1·125	Smeaton.
Mercury .	100	1·802	91	1·640	11	1·650	Dulong and Petit.

hese cases, owing partly, perhaps, to the dimorphism of sulphur, and to the impossibility of ascertaining which modification of this element may be present in the compound.

The sulphates are regarded by Kopp as consisting of M, SO_4. They are subdivided by him into two classes: in the first class, SO_4 is assumed to possess a volume = 186, in the second, a volume = 236. There is no simple relation between these two numbers; but if we view the sulphates as formed upon the plan MO, SO_3, and deduct from the numbers assigned by Kopp for SO_4, 32 as the atomic volume of an equivalent of oxygen (adding it in all cases to the numbers which represent the atomic volume of the metal in the salt); the numbers which represent SO_3 in the two classes will be 154 and 204. Now by substituting 153 for 154, we may represent the two volumes of SO_3 by numbers which are in the ratio of 3 : 4, and if this slight alteration be adopted, the atomic volumes obtained by calculation agree as well with those furnished by experiment as those which have been calculated by Kopp.

In the chromates, the tungstates, the carbonates, and the nitrates, but a single class has been recognised for each acid :—

Name of salt. (Formula MO,SO_3)	Eqt.No. O = 100.	Calculated Atomic Volume.	Calcul. Sp. gr.	Observed Specific Gravity.
		SULPHATES, CLASS I. SO_3 = 153.		
Lead . . .	1895	146 + 153 = 299	6·32	6·30, Mohs, Filhol; 6·17, Karsten.
Baryta . .	1458	175 + 153 = 328	4·44	4·45, Mohs; 4·20, Karsten.
Potash . .	1087	266 + 153 = 419	2·59	2·62, Karsten, Filhol; 2·66, Kopp; 2·64, Playfair and Joule.
Strontia . .	1148	140 + 153 = 293	3·92	3·59, Karsten; 3·77, Filhol; 3·95, Breithaupt.
		SULPHATES, CLASS II. SO_3 = 204.		
Copper . .	997	76 + 204 = 280	3·56	3·53, Karsten, Filhol; 3·631, Playfair and Joule.
Silver . .	1950	160 + 204 = 364	5·35	5·34, Karsten; 5·41, Filhol; 5·322, Playfair and Joule.
Zinc . . .	1006	89 + 204 = 293	3·43	3·40, Karsten, Filhol; 3·681, Playfair and Joule.
Lime . . .	850	92 + 204 = 296	2·89	2·93, Karsten; 3·102, Filhol; 2·96, Naumann.
Magnesia .	750	72 + 204 = 276	2·71	2·61, Karsten; 2·628, Filhol; 2·706, Playfair and Joule.
Soda . . .	888	162 + 204 = 366	2·42	2·63, Kopp; 2·629, Filhol; 2·597, Playfair and Joule.
MO,CrO_3.		CHROMATES, CrO_3 = 196.		
Lead . . .	2022	146 + 196 = 342	5·91	5·95, Breithaupt; 6·00, Mohs; 5·653, Playfair and Joule.
Potash . .	1215	266 + 196 = 462	2·63	2·64, Karsten; 2·74, Kopp; 2·682, Playfair and Joule.
Silver . .	2078	160 + 196 = 356	5·83	5·77, Playfair and Joule.
MO,WO_3.		TUNGSTATES, WO_3 = 212.		
Lead . . .	2844	146 + 212 = 358	7·94	8·0, Gmelin; 8·1, Leonhard.
Lime . . .	1800	92 + 212 = 304	5·92	6·04, Karsten; 6·03, Meissner.

Carbonates. $CO_2 = 119$.

Name of Salt. (Formula MO,CO_2)	Eqt. No. $O=100$.	Calculated Atomic Volume.	Calcul. Sp. gr.	Observed Specific Gravity.
Cadmium .	1073	$113+119=232$	4·63	4·42, Herapath; 4·49, Kopp.
Iron . . .	725	$76+119=195$	3·72	3·829, Mohs; 3·872, Naumann.
Lead . . .	1670	$146+119=265$	6·30	6·43, Karsten; 6·47, Breithaupt.
Manganese .	722	$76+119=195$	3·70	3·55—3·59, Mohs.
Silver . .	1725	$160+119=279$	6·18	6·08, Karsten.
Zinc . . .	781	$89+119=208$	3·75	4·44, Mohs; 4·4—4·5, Naumann.
Baryta . .	1233	$175+119=294$	4·19	4·30, Karsten, Mohs; 4·24, Breithaupt; 4·565, Filhol.
Lime . . .	625	$92+119=211$	2·96	3·00, (Aragonite) Breithaupt; 2·93, Mohs; 2·70 (Iceland spar), Karsten; 2·72, Beudant.
Magnesia .	525	$72+119=191$	2·75	2·81, Breithaupt; 3·0—3·11, Mohs.
Potash . .	862	$266+119=385$	2·24	2·26, Karsten; 2·267, Filhol; 2·103, Playfair and Joule.
Soda . . .	662	$162+119=281$	2·38	2·47, Karsten; 2·509, Filhol; 2·427, Playfair and Joule.
Strontia . .	923	$140+119=259$	3·56	3·60, Mohs; 3·62, Karsten.
(MO,NO_5).				Nitrates. $NO_5 = 326$.
Lead . . .	2069	$146+326=472$	4·32	4·581, Filhol; 4·40, Karsten; 4·34, Kopp; 4·316, Playfair and Joule.
Silver . .	2125	$160+326=486$	4·37	4·36, Karsten; 4·336, Playfair and Joule.
Ammonia .	1000	$250+326=576$	1·71	1·74, Kopp; 1·635, Playfair and Joule.
Baryta . .	1634	$175+326=501$	3·26	3·200, Filhol; 3·19, Karsten; 3·284, Playfair and Joule.
Lime . . .	1025	$92+326=418$	2·45	2·240, Filhol.
Potash . .	1263	$266+326=592$	2·12	2·10, Karsten; 2·06, Kopp; 2·07, Playfair and Joule.
Soda . . .	1063	$162+326=488$	2·19	2·260, Filhol, Karsten; 2·19, Marx; 2·20, Kopp; 2·182, Playfair and Joule.
Strontia . .	1324	$140+326=466$	2·84	2·857, Filhol; 2·84, Karsten; 2·704, Playfair and Joule.

(1472) 3. *Volumes of Compounds in Solution.*—A series of interesting researches was made a few years ago by Playfair and Joule upon the bulk occupied by the equivalent quantities of different solid compounds, compared with that which they occupy when in solution (*Phil. Mag.*, 1845, vol. xxvii.). Some of these results are included in the table (page 774), in which they are all referred to the quantity of water in grains which an equivalent in grains of each substance ($H=1$) would displace when immersed in water.

The quantity of water displaced is easily calculated by dividing the equivalent number of the substance by its specific gravity. It was in these cases determined experimentally by taking a given weight, say an equivalent in grains, of the substance under trial, and introducing it into the volumenometer, described at page 765.

When known quantities of different salts were brought into solution, and the increase of bulk in the liquid thus produced was ascertained, it was found—1. That a salt when in solution always ccupies less space than it did when in the solid state.—2. That quivalent quantities of different salts when in solution occupy ither the same volume, or volumes which are simple multiples or ubmultiples of each other.* If 9 (the equivalent volume of water) e assumed as the standard of comparison, an equivalent of the ifferent salts, when dissolved in water, increases the volume of the liquid by 9, or by some multiple of 9. For instance, 87 grains or 1 equivalent of sulphate of potash in its dry state, displaces 33 grains of water, but it increases the bulk of the liquid by only 18 grain measures when in solution; 101 grains of nitrate of potash in the solid form displace 48 grains of water, but when in solution they displace 36 grains. In the case of carbonate of potash the condensation is still greater; for 69 grains of the solid salt occupy a space of 39 water grains, and of 9 only when in solution. It is, however, necessary to remark that the volume occupied by the salt when in solution is somewhat influenced by the degree of saturation of the liquid, the increase of volume being slightly greater when the solution approaches the point of saturation. Thus it was found in the case of cane sugar, that when an equivalent of sugar (171 grains) was dissolved in different amounts of water, the increase in volume of the solution was as follows :—

Sugar.		Water.	Temperature.	Atomic Volume in grain Measures of Water.
1	:	120	60°	99·00
1	:	10	52°	105·09
1	:	1	52°	107·01
3	:	1	52°	108·06

3. That when a salt usually crystallizes with a large proportion of water of crystallization, such salt, when reduced to the anhydrous state, may be dissolved in water without increasing its bulk.†

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* The atomic volume of a salt in solution, however, varies considerably with the temperature, and increases rapidly as the temperature rises, so that it is only at a particular temperature for each salt that this law holds true. Thus the solution volume of an equivalent of each of the following salts is for—

Sulphate of zinc . .	$ZnO, SO_3, 7 Aq$,	at 32° = 56·1	at 90° = 63
„ magnesia	$MgO, SO_3, 7 Aq$,	at „ = 60·8	at 85° = 63
„ iron . .	$FeO, SO_3, 7 Aq$,	at „ = 61·0	at 80° = 63.

† This observation was originally made by Dalton, but he supposed that in all cases when a salt was dissolved in water, the bulk of the liquid was unaltered, except by the bulk of water which the salt might contain.

For example, anhydrous carbonate of soda, and the anhydrous sulphates of soda and of magnesia, may be brought into solution without adding to the bulk of the liquid. If the salts be dissolved in their hydrated form, they increase the bulk of the liquid solely by the number of grains of water of crystallization which they contain: thus 143 grains, or one equivalent in grains of crystallized carbonate of soda, or 161 grains of the crystallized sulphate of soda, each of which contains 90 grains, or 10 equivalents of water of crystallization, causes an increase of 90 grain measures in the bulk of the water in which it is dissolved; 123 grains, or an equivalent of sulphate of magnesia, containing 7 equivalents or 63 grains of water, occasions an increase of 63 grain measures of water when brought into solution.

Volumes in grains of water of an equivalent in grains of several anhydrous salts, both when dry and when in solution (H = 1).

Name of the Metal.	Chloride.		Bromide.		Iodide.		Sulphate.		Nitrate.		Carbonate.	
	Dry.	Solution.	Dry.	Solution.	Dry.	Solution.	Dry.	Solution.	Dry.	Solution.	Dry.	Solution.
Potassium .	39·3	26·8	44·0	28·8	54·2	44·0	33·0	18·0	48·9	36·1	33·0	9.2
Sodium . .	29·2	18·3	...	19.0	...	...	27·5	1·6	39·1	26·5	22·0	0
Ammonium	34·0	35·7	...	...	...	...	...	27·0	49·1	45·5	...	...
Calcium .	22·5	1·6	...	...	...	...	23·4	...	...	...	...	...
Strontium .	...	0	...	...	...	...	...	...	39·2	26·5	...	...
Barium . .	...	9·8	...	...	...	...	23·9	...	39·8	27·0	...	...
Magnesium	22·1	2·0	...	...	...	...	22·5	0	...	18·8	...	...
Zinc . . .	...	...	...	...	...	...	21·85	0	...	...	...	...
Iron . . .	...	...	...	...	...	...	24·0	0	...	...	...	...
Cobalt . .	22·1	...	...	...	...	...	22·0	..	...	...	...	...
Copper . .	22·0	8·1	...	...	...	...	22·0	0	...	18·2	...	...
Lead . .	24·5	...	...	...	...	...	24·1	...	38·4	25·4	...	...
Mercury .	22·0	18·4	...	...	...	...	...	...	...	...	...	...
Silver . .	2 ·1	...	...	...	...	...	29·4	...	39·2	27·2	...	...

(1473) 4. *Atomic Volumes of Liquids of Analogous Composition.*—In the year 1842 an important paper was published by Kopp (Liebig's *Annal.* xli. 79, 169), in which he showed that when liquids belonging to one homologous series are compared with corresponding terms of other collateral homologous series (*vide* table, p. 32), like differences are observed in their atomic volumes. When, for instance, the atomic volume of a hydrated acid (HO, A) (A representing an equivalent of any monobasic anhydrous acid) is compared with its corresponding vinic ether (C_4H_5O, A), the atomic volume of the hydrated acid, at ordinary temperatures, is about 534 less than that of the corresponding compound ether.

The atomic volume of the hydrated acid (HO, A) is about 300 less than that of its corresponding methylic compound (C_2H_3O, A); and as a necessary consequence, the atomic volume of an ethylic compound is about 234 greater than that of the corresponding methylic compound. A more careful examination of the subject has shown that the somewhat considerable divergences observed between the atomic volumes calculated according to these laws, and those actually found by observation, are materially reduced if the liquids be compared, not at *equal* temperatures, but at *corresponding* temperatures. Corresponding temperatures are those at which the cohesion of the liquids compared is equal; or temperatures at which the liquids emit vapours of equal tension. The tension of the vapours of different liquids through the required range of the thermometric scale is, however, only known in a few instances; but it may be assumed without any very serious error, that corresponding temperatures in liquids are those situated at equal distances below the boiling points of the liquids under comparison. Thus, if the boiling point of alcohol be 173°, and if that of ether be 94°, the temperature of 60° F. would not be a corresponding temperature for these liquids; but if the alcohol be at 60°, which is 113° below its boiling point, the corresponding temperature for ether would be 113° below its boiling point, or —19°.

The atomic volume v of a compound increases as the temperature rises. This, indeed, must be evident from the consideration that the specific gravity d diminishes as the temperature rises, whilst the equivalent number q remains constant; and since $\frac{q}{d} = v$, the atomic volume must necessarily vary inversely as the density of the body, and consequently must increase as the temperature rises. In making comparisons of atomic volumes of compounds it is found advantageous in practice always to calculate them for the boiling point of the respective liquids under a pressure equal to that of 30 inches of mercury.

At the time when Kopp first called attention to the atomic volume of liquids, few really exact data existed, by means of which his conclusions could be rigidly tested. Since that period both Pierre (*Ann. de Chimie*, III. xv. 325; xix. 193, and xx. 5.) and Kopp himself (Poggendorff's *Annal.* lxxii. 1 and 223, Liebig's *Annal.* xciv. 257, xcv. 307), have published a series of important and elaborate researches upon the specific gravity, the expansion, and the boiling points of a considerable number of liquids, by means of which the atomic volume of these liquids at the boiling point

may be calculated. The following table contains the results
Kopp's inquiries arranged for the convenience of comparison :—

Name of Compound.	Formula.	Eqt. O=100	Sp. gr. at 32°.	Calc. boiling point, ° F.	Atomic volume at boiling.	Diff. in at. vol. for C_2H_2.	M diff C
Water	H_2O_2	225	1·000	212·0	235·0		
Wood spirit . .	C_2H_3O, HO	400	0·8147	138·2	527·5	292·5	
Alcohol	C_4H_5O, HO	575	0·8095	172·4	781·0	253·5	2
Fousel oil . . .	$C_{10}H_{11}O, HO$	1100	0·8253	275·0	1550·0	3×256	
Carbolic acid . .	$C_{12}H_5O, HO$	1175	1·0808	381·2	1300·0		
Benzo-alcohol .	$C_{14}H_7O, HO$	1350	1·0628	415·4	1546·0	246	
Formic acid . . .	HO, C_2HO_3	575	1·2227	210·2	522·5		
Acetic acid . . .	$HO, C_4H_3O_3$	750	1·0620*	244·4	797·5	275·0	
Propionic acid . .	$HO, C_6H_5O_3$	925	1·0161	278·6	1067·5	270·0	27
Butyric acid . .	$HO, C_8H_7O_3$	1100	0·9886	312·8	1347·5	280·0	
Valeric acid . .	$HO, C_{10}H_9O_3$	1275	0·9555	347·0	1640·0	292·5	
Benzoic acid . .	$HO, C_{14}H_5O_3$	1525	1·0838†	487·4	1586·0		
Acetic anhydride .	$C_4H_3O_3, C_4H_3O_3$	1275	1·0969	280·4	1375·0		
Ether	$C_8H_{10}O_2$	925	0·7366	93·2	1325·0		
Formiate of methyl	C_2H_3O, C_2HO_3	750	0·9984	96·8	782·5		
Acetate of methyl	$C_2H_3O, C_4H_3O_3$	925	0·9562	131·0	1060·0	277·5&	
Formiate of ethyl	C_4H_5O, C_2HO_3	925	0·9394	131·0	1068·7	286·2	
Acetate of ethyl .	$C_4H_5O, C_4H_3O_3$	1100	0·9105	165·2	1345·0	285·0&	
Butyrate of methyl	$C_2H_3O, C_8H_7O_3$	1275	0·9210	199·4	1581·2	276·3	
Propionate of ethyl	$C_4H_5O, C_6H_5O_3$	1275	0·9231	199·4	1572·5	236·2	
Valerate of methyl	$C_2H_3O, C_{10}H_9O_3$	1450	0·9015	233·6	1865·0		28
Butyrate of ethyl	$C_4H_5O, C_8H_7O_3$	1450	0·9041	233·6	1865·0		
Acetate of tetryl	$C_8H_9O, C_4H_3O_3$	1450	0·9004	233·6	1866·2		
Formiate of amyl	$C_{10}H_{11}O, C_2HO_3$	1450	0·8945	233·6	1872·5		
Valerate of ethyl	$C_4H_5O, C_{10}H_9O_3$	1625	0·8829	267·8	2168·7		
Acetate of amyl	$C_{10}H_{11}O, C_4H_3O_3$	1625	0·8837	267·8	2166·0		
Valerate of amyl .	$C_{10}H_{11}O, C_{10}H_9O_3$	2150	0·8793	370·4	3051·0		
Benzoate of methyl	$C_2H_3O, C_{14}H_5O_3$	1700	1·1026	374·0	1879·0		
Benzoate of ethyl .	$C_4H_5O, C_{14}H_5O_3$	1875	1·0657	408·2	2185·0	306·0	30
Benzoate of amyl .	$C_{10}H_{11}O, C_{14}H_5O_3$	2400	1·0039	510·8	3096·0	3×303·7	
Cinnamate of ethyl	$C_4H_5O, C_{18}H_7O_3$	2200	1·0656	500·0	2641·2		
Salicylate of methyl	$C_2H_3O, C_{14}H_5O_5$	1900	1·1969	433·4	1867·5		
Carbonate of ethyl	$C_8H_{10}O_2, C_2O_4$	1475	0·9998	258·8	1738·7		
Oxalate of methyl	$C_4H_6O_2, C_4O_6$	1475	1·1566‡	323·6	1453·7		
Oxalate of ethyl .	$C_8H_{10}O_2, C_4O_6$	1825	1·1016	366·8	2087·5	2×316·9	
Succinate of ethyl	$C_8H_{10}O_2, C_8H_4O_6$	2175	1·0718	422.6	2612·5		
Acetone	$C_6H_6O_2$	725	0·8144	132·8	966·2		
Aldehyd	$C_4H_4O_2$	550	0·8009	69·8	711·2	255·0	
Valeraldehyd . .	$C_{10}H_{10}O_2$	1075	0·8224	213·8	1499·8	3×262	
Hydride of benzoyl	$C_{14}H_6O_2$	1325	1·0636	354·2	1480·0		
Hydride of cumyl	$C_{20}H_{12}O_2$	1850	0·9832	456·8	2365·0	3×295	
Benzole	$C_{12}H_6$	975	0·8991	176·0	1200·0		
Cymole	$C_{20}H_{12}$	1675	0·8778	347·0	2307·5	4×277	
Naphthalin . . .	$C_{20}H_8$	1600	0·9774§	424·4	1890·0		
Tetryl	$C_{16}H_{18}$	1425	0·7135	226·4	2306·2		

(1474) The atomic volumes given in the foregoing table are those calculated by Kopp, for the *boiling point* of their respective iquids given in the fifth column of the table. These boiling points are not in all cases the actual numbers obtained by experiment, but are in some instances modified according to considerations explained in (1475), since the boiling point of many substances is only approximatively known, the estimates of different observers sometimes varying several degrees. The atomic volumes contained in this table, therefore, differ from the earlier calculations already referred to, which were all made at ordinary temperatures. Now, it appears, if we compare the hydrated acids contained in Division II. of the table with the ethers in Division III., that the atomic volume of the hydrated acid is about 537 less than that of the corresponding ether; for instance:—

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* At 63°. † At 250°. ‡ At 122°. § At 175°.

	At. Vol.		At. Vol.		At. Vol.
Butyric ether	= 1865·0	Acetic ether	= 1345·0	Formic ether	= 1068·7
Butyric acid	= 1347·5	Acetic acid	= 797·5	Formic acid	= 522·5
Difference	517·5		547·5		546·2

The difference between the atomic volume of the hydrated acid and that of its corresponding methylic compound is about 252:—

Butyr. methyl	= 1581·2	Acet. methyl	= 1060·0	Form. methyl	= 782·5
Butyric acid	= 1347·5	Acetic acid	= 797·5	Formic acid	= 522·5
	233·7		262·5		260·0

and, as may be seen by inspection of the table, the mean difference between the atomic volume of the corresponding compounds in the ethyl and the methyl series is about 292:—

Valer. ethyl	= 2170·0	Butyr. ethyl	= 1865·0	Acet. ethyl	= 1345
Valer. methyl	= 1865·0	Butyr. methyl	= 1581·2	Acet. methyl	= 1060
	305·0		283·8		285·0

Now, since the corresponding compounds of the ethylic and the methylic series differ by (C_2H_2) this mean difference in the atomic volume of such corresponding compounds has been assumed by Kopp to represent the volume occupied by each equivalent of (C_2H_2) when in combination. This difference, it will be seen from the foregoing table, ranges in a large number of compounds between 250 and 300. Kopp fixes 275 as its average value at the boiling point of each compound.

Isomeric liquids of analogous composition, such, for instance, as the different metameric compound ethers, possess atomic volumes which are sensibly equal to each other; such, for instance, as:—

Butyric acid	$HO, C_8H_7O_3 = 1347{\cdot}5$	Valer. methyl	$C_4H_6O, C_{10}H_9O_3 = 1865$
Acetic ether	$C_4H_5O, C_4H_3O_3 = 1345$	Butyr. ethyl	$C_2H_3O, C_8H_7O_3 = 1865$

Numerous other cases may also be seen by comparing the volumes of the ethers which are bracketed together in the table, p. 776. But if the isomeric compounds belong to different and dissimilar series, the same correspondence is not observed; for example:—

Acetone . . .	$(C_6H_6O_2)_2$=1932·4	Aldehyd . .	$(C_4H_4O_2)_2$=1422·4
Valerate of methyl	$C_2H_3O,C_{10}H_9O_3$=1865·0	Butyric acid	$HO,C_8H_7O_3$ =1347·5
	67·4		74·9

By comparing together liquids which contain the same number of equivalents, but in which a certain number of equivalents of oxygen have been substituted for a similar number of equivalents of hydrogen, it is found, contrary to an opinion formerly expressed by Kopp, that the atomic volume of oxygen is somewhat greater than that of hydrogen; as for example:—

Acetic anhydride	$C_8H_6O_6$=1375·0	Acetic acid . . .	$C_4H_4O_4$=797·5
Butyric acid . .	$C_8H_8O_4$=1347·5	Alcohol	$C_4H_6O_2$=781·0
	27·5		16·5

From a similar comparison of compounds in which a certain number of equivalents of carbon have taken the place of an equal number of equivalents of hydrogen, it has been concluded that the volumes of carbon and of hydrogen are equal. This is exemplified, according to Kopp, in the corresponding compounds of the valeric ($C_{10}H_{10}O_4$), and the benzoic ($C_{14}H_6O_4$) acids; but the examples which he has selected to prove this point indicate that there is a slight difference in the volumes of the two elements; thus—

Benzoate of methyl	= 1879	Benzoic ether	= 2185	Benzoate of amyl	= 3096
Valerate of methyl	= 1865	Valeric ether	= 2170	Valerate of amyl	= 3051
	14		15		45

For the further prosecution of this subject the reader is referred to Kopp's interesting papers in Liebig's *Annalen*, Bd. xcv. and xcvi.

The general conclusion which it appears we are at present warranted in drawing from these observations is the following:—That in homologous compounds there is a definite and constant difference in their atomic volume corresponding to each successive addition of C_2H_2, but that the number which expresses this constant difference in one class of compounds differs from that which expresses it in other classes of homologous compounds.

(1475) *Kopp's Law of the Boiling Points.*—At the same time that Kopp pointed out the regular increase in atomic volume which the successive terms of the same homologous series exhibit, he called attention to a not less remarkable regularity in the increase of the temperature required to produce ebullition as the number of equivalents of (C_2H_2) increases in the compound. By inspecting the table at p. 776 Div. III., it will be seen on comparing the boiling points of the compounds of ethyl and of methyl, that for every addition of C_2H_2 in the empirical formula, a rise in the boiling point of about 36° F. takes place.

The rise of temperature for each additional equivalent of C_2H_2 differs, however, in different classes of homologous compounds, as may be seen by an examination of the following table, from which it appears that in the *alcohols* the mean elevation of the boiling point for C_2H_2 is 31°·4. In the *aldehyds* it is 47°, though in this class the divergences from the mean are so considerable that it is probable that several of the assigned boiling points are inaccurate. In the *radicles of the alcohols* the mean rise is 42°, and in the *homologues of benzole* it is 41°. In the *acids* of the acetic series it is 38°·9, and in the aniline *bases* it is 30°·5.

Ethers.	Formula.	Observed Boiling Point.
Methylic ether . .	$C_4H_6O_2$	−5°·8, Berthelot.
Methylethylicether	$C_6H_8O_2$	+51°·8, Williamson.
Ethylic ether . .	$C_8H_{10}O_2$	93°·2, Dumas; 93°·5, Kopp; 94°·8, Andrews; 95°, Delffs; 95·9, Pierre; 96·3, Gay Lussac.
Methyl amylic ether	$C_{12}H_{14}O_2$	161°·6, Williamson.
Ethyl tetrylic ether	$C_{12}H_{14}O_2$	172°·4—176°, Wurtz.
Ethyl amylic ether	$C_{14}H_{16}O_2$	233°·6, Williamson.
Tetrylic ether . .	$C_{16}H_{18}O_2$	212°—219°·2? Wurtz.
Amylic ether . .	$C_{20}H_{22}O_2$	231°·8—233°·6? Balard; 338°·0, Gaultier; 347°—361°, Rieckher.
	Mean difference for C_2H_2 = 44° F.	
Alcohols.		
Wood spirit . . .	$C_2H_4O_2$	148°—149°·2, Kopp; 140°, Kane; 140°·9—141°·8, Delffs.
Ethylic alcohol . .	$C_4H_6O_2$	172°·4—173°·8, Kopp; 172°·2, Andrews; 173°, Pierre; 173°·1, Gay Lussac.
Tritylic do.	$C_6H_8O_2$	204°·8, Chancel.
Tetrylic do. . . .	$C_8H_{10}O_2$	228°·2, Wurtz.
Amylic do. . . .	$C_{10}H_{12}O_2$	266°·7—271°·4, Kopp; 269°·4, Pierre; 269°·6, Delffs, Cahours.
Hexylic do.	$C_{12}H_{14}O_2$	298°—309°, Faget.
Heptylic do. . .	$C_{14}H_{16}O_2$	?
Octylic do. . . .	$C_{16}H_{18}O_2$	360°, Bouis; 352°·4, Moschnin.
	Mean difference for C_2H_2 = 31°·4 F.	
Aldehyds.		
Acetic.	$C_4H_4O_2$	71°·4, Liebig; 71°·6, Pierre; 67°·8, Kopp.
Propylic	$C_6H_6O_2$	131°—149°, Guckelberger.
Butylic	$C_8H_8O_2$	154°—167°, Guckelberger.
Valeric	$C_{10}H_{10}O_2$	199°·2, Kopp; 204°·8—206°·6, Parkinson; 206°·6, Limpricht.
Œnanthylic . . .	$C_{14}H_{14}O_2$	311°—316°·4, Bussy.
rylic	$C_{16}H_{16}O_2$	?
tic	$C_{20}H_{20}O_2$	446°, Gerhardt.
	Mean difference for C_2H_2 = 47° F.	

Acids.	Formula.		Observed Boiling Point.
Formic	$C_2H_2O_4$		209°·3, Liebig; 212°, Wurtz; 221°·7, Kopp.
Acetic.	$C_4H_4O_4$		240°·8, Delffs; 242°·4, Kopp.
Propionic . . .	$C_6H_6O_4$		286°·9, Kopp; about 284°, Dumas and others.
Butyric	$C_8H_8O_4$		312°·8, Kopp, Delffs; 325°·4, Pierre; 327°·2, Pelouze.
Valeric	$C_{10}H_{10}O_4$		346°·1, Delffs; 347°, Dumas and Stas; 348°·4, Kopp.
Caproic	$C_{12}H_{12}O_4$		388°·4, Brazier and Gossleth; 395°·6—408°, Fehling.
Œnanthylic . . .	$C_{14}H_{14}O_4$		?
Caprylic	$C_{16}H_{16}O_4$		456°·8, Fehling.
Pelargonic . . .	$C_{18}H_{18}O_4$		500°·0, Cahours.
	Mean difference for $C_2H_2 = 36°$.		
Anhydrides.			
Acetic	$C_8H_6O_6$		280°·4, Gerhardt, Kopp; 278°·6, Wurtz.
Propionic . . .	$C_{12}H_{10}O_6$		336°·2, Limpricht and Uslar.
Butyric	$C_{16}H_{14}O_6$		About 374°, Gerhardt.
Valeric	$C_{20}H_{18}O_6$		About 419°, Gerhardt.
Caprylic	$C_{32}H_{34}O_6$		About 554°, Chiozza.
	Mean difference for $C_2H_2 = 22°·7$.		
Methylic Ethers.			
Formiate of methyl	C_2H_3O, C_2HO_3		90°·8, Kopp; 91°·2, Andrews.
Acetate	$C_2H_3O, C_4H_3O_3$		131°, Andrews; 132°·3—132°·6, Kopp; 139°·1, Pierre.
Propionate . . .	$C_2H_3O, C_6H_5O_3$		?
Butyrate . . .	$C_2H_3O, C_8H_7O_3$		199°·4, Delffs; 203°—203°·2, Kopp; 215°·8, Pierre.
Valerate . . .	$C_2H_3O, C_{10}H_9O_3$		237°·2—240°·0, Kopp.
	Mean difference for $C_2H_2 = 37°·2$.		
Ethylic Ethers.			
Formiate of ethyl	C_4H_5O, C_2HO_3		127°·2, Pierre; 127°·4, Delffs; 128°, Liebig; 130°·5—131°·5, Kopp.
Acetate	$C_4H_5O, C_4H_3O_3$		164°·7, Kopp; 165°·2, Dumas, Delffs, Pierre.
Propionate . . .	$C_4H_5O, C_6H_5O_3$		204°·5—208°·4, Kopp; 213°·8, Limpricht and Uslar.
Butyrate . . .	$C_4H_5O, C_8H_7O_3$		230°, Lerch; 235°·4, Delffs; 237°·7, Kopp; 246°·2, Pierre.
Valerate . . .	$C_4H_5O, C_{10}H_9O_3$		268°·7, Delffs; 271°·8, Kopp; 272°·3, Otto; 271°·4—273°·2, Berthelot.
Caproate . . .	$C_4H_5O, C_{12}H_{11}O_3$		248°? Lerch; 323°·6, Fehling.
Pelargonate . .	$C_4H_5O, C_{18}H_{17}O_3$		420°·8—424°·4, Cahours; 435°·2 Delffs.
	Mean difference for $C_2H_2 = 38°·8$.		
Other Ethers.			
Acetate of trityl .	$C_6H_7O, C_4H_3O_3$	2 × 36	About 194°, Berthelot.
Butyrate of trityl	$C_6H_7O, C_8H_7O_3$		About 266°, do.
Formiate of tetryl	C_8H_9O, C_2HO_3	25·2	About 212°, Wurtz.
Acetate of tetryl .	$C_8H_9O, C_4H_3O_3$		237°·2, do.

Compound Ethers.	Formula.	Observed Boiling Point.
Formiate of amyl	$C_{10}H_{11}O, C_2\,H\,O_3$	237°·2, Delffs; about 240°·8, Kopp.
Acetate	$C_{10}H_{11}O, C_4\,H_3\,O_3$	271°·4, Delffs; 272°—279°·1, do.
Propionate . . .	$C_{10}H_{11}O, C_6\,H_5\,O_3$	About 311°·, Wrightson.
Valerate . . .	$C_{10}H_{11}O, C_{10}H_9\,O_3$	372°—372°·9, Kopp.
Caproate . . .	$C_{10}H_{11}O, C_{12}H_{11}O_3$	411°·8, Brazier and Gossleth.
Mean difference for C_2H_2 = 34°·9.		
Acetate of octyl .	$C_{16}H_{17}O, C_4\,H_3\,O_3$	379°·4, Bouis.
Laurate of ethyl .	$C_4\,H_5\,O, C_{21}H_{23}O_3$	507°, Georgey; 516°, Delffs.
Alcohol Radicles.		
Ethyl tetryl . .	$C_{12}H_{14}$	143°·6, Wurtz.
Methyl hexyl . .	$C_{14}H_{16}$	179°·6. do.
Ethyl amyl . .	$C_{14}H_{16}$	190°·4, do.
Tetryl	$C_{16}H_{18}$	222°·8, Wurtz; 226°·4, Kolbe; 227°·3, Kopp.
Tetryl amyl . .	$C_{18}H_{20}$	269°·6, Wurtz.
Amyl	$C_{20}H_{22}$	311°, Frankland; 316°·4, Wurtz.
Tetryl hexyl . .	$C_{20}H_{22}$	311°, Wurtz.
Hexyl	$C_{24}H_{26}$	395°·6, Brazier and Gossleth.
Mean difference for C_2H_2 = 42°.		
Hydrocarbons.		
Benzole	$C_{12}H_6$	176°·7, Kopp; 176°·9, Mansfield; 177°·6, Church.
Toluole	$C_{14}H_8$	218°·7, Church; 222°·8, Glenard and Boudault; 226°·4, Deville, Pelletier and Walter; 229°·1, Noad; 235°·4, Mansfield.
Xylole	$C_{16}H_{10}$	259°·1, Church; 264°·2, Cahours.
Cumole	$C_{18}H_{12}$	298°·4, Abel; 299°·1, Church; 304°·5, Gerhardt.
Cymole	$C_{20}H_{14}$	339°·2, Church; 339°·8, Mansfield; 340°·7, Noad; 351°·5, Kopp.
Mean difference for C_2H_2 = 41°.		

In the homologous ethers, which contain chlorine, bromine, iodine, and sulphur, the difference in the boiling point produced by each successive addition of C_2H_2 is considerably higher than in the compound ethers. For example:—

Compounds.	Formula.	Difference.	Observed Boiling Point.
Chloride of methyl	$C_2\,H_3\,Cl$		— 4°·, Berthelot.
Chloride of ethyl .	$C_4\,H_5\,Cl$	55°·8	+ 51°·8, Pierre.
Chloride of tetryl .	$C_8\,H_9\,Cl$	2 × 52°·5	158°—167°, Wurtz.
Chloride of amyl .	$C_{10}H_{11}Cl$	48	215°·6, Pierre, Cahours.
Chloride of octyl .	$C_{16}H_{17}Cl$	43	347°, Bouis.
Mean difference for C_2H_2 = 50°.			
Bromide of methyl	$C_2\,H_3\,Br$	50	55°·4, Pierre.
Bromide of ethyl .	$C_4\,H_5\,Br$		105°·8, do.
Bromide of tetryl .	$C_8\,H_9\,Br$	2 × 43°·2	192°·2, Wurtz.
Bromide of amyl .	$C_{10}H_{11}Br$	54	246°·2, Pierre.
Bromide of octyl .	$C_{16}H_{17}Br$	43	374°, Bouis.
Mean difference for C_2H_2 = 45°·5.			

Compounds.	Formula.	Difference.	Observed Boiling Point.
Iodide of methyl .	$C_2 H_3 I$		107°·6, Andrews; 111°·2, Pierre.
Iodide of ethyl .	$C_4 H_5 I$		158°·0, Pierre; 159°·8, Andrews; 161°·6, Frankland.
Iodide of tetryl .	$C_8 H_9 I$		249°·8, Wurtz.
Iodide of amyl .	$C_{10}H_{11}I$		294°·8, Frankland; 298°·4, Kopp; 300°, Grimm.
Iodide of octyl .	$C_{16}H_{17}I$		410°, Bouis.
	Mean difference for $C_2H_2 = 43°$.		
Sulphide of methyl	$C_4 H_6 S_2$		105°·8, Regnault.
Sulphide of ethyl .	$C_8 H_{10}S_2$	2×45	195°·8, Pierre.
Sulphide of amyl .	$C_{20}H_{22}S_2$	6×37	420°·8, Balard.
	Mean difference for $C_2H_2 = 40°$.		
Methyl mercaptan	$C_2 H_3 S, HS$		69°·8? Gregory.
Ethyl mercaptan .	$C_4 H_5 S, HS$	27?	96°·8, Liebig.
Tetryl mercaptan	$C_8 H_9 S, HS$	2×46°·8	190°·4, Humann.
Amyl mercaptan .	$C_{10}H_{11}S, HS$	57°·6	242°6, Krutsch; 248°, Kopp.
	Mean difference for $C_2H_2 = 50°$.		

Bases.	Formula.	Observed Boiling Point.
Aniline	$C_{12}H_7 N$	359°·6, Hofmann.
Toluidine . . .	$C_{14}H_9 N$	388°·4, Muspratt and Hofmann.
Xylidine	$C_{16}H_{11}N$	?
Cumidine . . .	$C_{18}H_{13}N$	437°, Nicholson.
Cymidine . . .	$C_{20}H_{15}N$	482°, Barlow.
	Mean difference for $C_2H_2 = 30°·5$.	
Pyridine	$C_{10}H_5 N$	240°, Anderson
Picoline	$C_{12}H_7 N$	271°·4, do.
Lutidine	$C_{14}H_9 N$	310°, do.
Collidine	$C_{16}H_{11}N$	356°, do.
	Mean difference for $C_2H_2 = 38°·7$.	

A comparison of metameric bodies of analogous composition shows that the boiling points of such compounds coincide very nearly, whereas if they belong to series which differ in their composition, the boiling points may vary widely. The differences between the hydrated acids and the compound ethers metameric with them, given in the table p. 780, show the latter point very clearly.

Many of the differences observed between the boiling points obtained by experiment and the theoretical numbers, (calculated according to Kopp's law of a constant difference,) may possibly disappear when the boiling points shall have been more accurately determined: but Kopp observes, that it must not be assumed that the boiling points of liquids, when compared at *any* given pressure, will always exhibit the same differences as they do when compared at the average pressure of 30 inches of mercury. It does not follow, for instance, though the boiling point of ether is 79°·5 below that of alcohol, under a pressure of 30 inches, that under a pressure of 15 inches, the difference between these boiling points should still be 79°·5: since it is well known that what is called Dalton's law (177), viz., that 'all liquids at equal distances from their boiling point, emit vapours of equal tension,' is not correct.

The accurate determination of the boiling point of a liquid is by no means easy, as might be inferred from an inspection of the foregoing tables, where many experimentalists of great skill and experience give for the same well-known substances, numbers which differ by several degrees from each other. Indeed, it has been found, independently of the irregular manner in which many liquids boil in glass vessels (167), that in several cases impurities so slight as not materially to affect the result of ultimate analysis of the substance, may yet produce a considerable effect upon its boiling point.

Numerous attempts have been made to determine the effect which the addition or the removal of a certain number of equivalents of each of the elements, carbon, hydrogen, and oxygen, exerts upon the boiling point of the resulting compound. These attempts, however, have not led to any satisfactory result, since the compounds thus compared belong generally to different series. The aldehyds, for example, cannot satisfactorily be compared with the alcohols, and it is only in the same homologous series that an equal rise in the boiling point can be expected for equal increments in the number of the constituent elements.

In the case of the alcohols, the volatile acids, and the compound ethers, Kopp, assuming a constant difference of 34°·2 F. for C_2H_2, has calculated a table of boiling points which approximate pretty closely to the observed numbers, the mean of the best observations of which are contrasted with Kopp's calculated numbers, in the following table:—

Alcohols.			Acids.			Compound Ethers.		
$C_nH_{n+1}O, +HO.$	Observed.	Calculated.	$HO + C_nH_{n-1}O_3.$	Observed.	Calculated.	$C_nH_{n+1}O + C_nH_{n-1}O_3.$	Observed.	Calculated.
$C_2H_4O_2$	140°·5	138°·2	$C_2H_2O_4$	210°·6	210°·2			
$C_4H_6O_2$	173°·0	172°·4	$C_4H_4O_4$	241°·6	244°·4	$C_4H_4O_4$	91°·0	96°·8
$C_6H_8O_2$	204°·8	206°·6	$C_6H_6O_4$	285°·5	278°·6	$C_6H_6O_4$	131°·8	131°·0
$C_8H_{10}O_2$	228°·2?	240°·8	$C_8H_8O_4$	312°·8	312°·8	$C_8H_8O_4$	165°·0	165°·2
$C_{10}H_{12}O_2$	269°·5	275°·0	$C_{10}H_{10}O_4$	347°·2	347°·0	$C_{10}H_{10}O_4$	201°·3	199°·4
$C_{12}H_{14}O_2$	309°·0	309°·2	$C_{12}H_{12}O_4$	388°·4	381°·2	$C_{12}H_{12}O_4$	236°·5	233°·6
$C_{14}H_{16}O_2$	?	343°·4	$C_{14}H_{14}O_4$	?	415°·4	$C_{14}H_{14}O_4$	270°·9	267°·8
$C_{16}H_{18}O_2$	360°·0	377°·6	$C_{16}H_{16}O_4$	456°·8	449°·6	$C_{16}H_{16}O_4$	311°·?	302°·0

If the calculated results given in the foregoing table be assumed to be accurate, it follows, if one of the bodies contained in this table be compared with others analogous to it in composition, that the boiling point will be raised by about 26°·1 for each additional equivalent of carbon; and that it will be reduced by about 26°·1, for a diminution of each equivalent of carbon; but the effect produced by hydrogen is the reverse of that produced by carbon; since for every additional equivalent of hydrogen, the boiling point is lowered 9°; and for every equivalent of hydrogen which is removed, it is raised 9°.

The reader will find an admirable digest of this subject by Kopp, in Liebig's *Annalen,* Bd. xcvi.

§ II. Atomic Heats.

(1476) *Relation of Specific Heat to Chemical Equivalents.*— An interesting relation has been traced between the specific heats of bodies and their combining quantities. It has already been stated (161) that the amount of heat required to raise equal weights of different substances 1° in temperature varies for each species of matter, but is always constant for the same body when it is placed under like circumstances. The numbers which represent the respective quantities of heat required to raise each substance, through a given number of degrees of the thermometric scale, when referred to that required to raise an equal weight of water, through the same interval of temperature, constitute the specific heats of the different bodies.

By comparing together quantities of the various elementary substances in the ratio of their chemical equivalents, and ascertaining the amount of heat which each requires to raise it through equal intervals of temperature, Dulong and Petit made the important observation that the quantities of heat absorbed bear a very simple numerical relation to each other. In a large proportion of instances, the amounts of heat thus absorbed, allowing for unavoidable errors of experiment, are identical; and it was further observed, that the exceptional cases nearly always exhibit some simple multiple relation to this number. In other words, *the specific heat of an elementary body is inversely as its chemical equivalent:* consequently, the product of the specific heat of an element into its equivalent number gives, within certain limits for errors of experiment, either a constant number, or some multiple of that number.

The law thus announced by Dulong and Petit has been confirmed by the subsequent researches of Regnault upon specific heat (*Ann. de Chimie,* II. lxxiii. 61, III. i. 129, and ix. 322). Regnault determined the specific heats of a great variety of bodies, both simple and compound. He designates the product obtained by multiplying the specific heat of a body by its chemical equivalent, as the *atomic heat* of the body.

In 17 of the simple bodies which he examined, most of which were in a state of chemical purity, he found the atomic heat to range between 3·31 and 2·82, with a mean of 3·13. The elements comprised in this class are the following—viz., aluminum, bismuth, cadmium, cobalt, copper, iron, lead, mercury, nickel, osmium, platinum, rhodium, selenium, sulphur, tellurium, tin, and zinc. A second smaller class was found to have an atomic heat which was double that of the elements contained in the foregoing list. It comprised silver and gold, antimony, arsenic and phosphorus, bromine and iodine, as well as potassium and sodium. These bodies gave for their atomic heat, numbers ranging between 5·85 and 6·87, with a mean of 6·42. Regnault has therefore proposed to divide by two, the numbers usually given as the equivalents of the elements in the second list.

The table which follows includes some of the principal results derived from Regnault's experiments, on a large number of elementary bodies. He found that the same element has a different specific heat if examined in a different state of aggregation: thus planished copper has a smaller specific heat than the same metal after having been annealed. The same fact is exhibited in dimorphous bodies, the densest form having the lowest specific heat: diamond for example, has a specific heat of 0·1468, whilst graphite has a specific heat one-third higher, or 0·2018; and the specific heat of wood charcoal is still higher, viz., 0·2415.

Specific and Atomic Heats of the Elements.

Elements.	Sp. Heat.	Equivalent.	Atomic Heat. (Sp. Heat × Eqt.)
Diamond	0·1468	6	0·8808
Graphite	0·2018	,,	1·2108
Wood charcoal . . .	0·2415	,,	1·4490
Sulphur.	0·20259	16	3·2414
Selenium	0·0837	39.6	3·3145
Tellurium	0·04737	64	3·031
Zinc	0·09555	32·5	3·1054
Aluminum	0·2143	13·7	2·9359
Iron	0·11379	28	3 1861
Nickel	0·10863	29·5	3·2045
Cobalt	0·10696	29·5	3·1553
Cadmium :	0·05669	55·7	3·1618

Specific and Atomic Heats of the Elements.

[*Continued.*]

Elements.	Sp. Heat.	Equivalent.	Atomic Heat. (Sp. Heat × Eqt.)
Tin	0·05623	58·8	3·2863
Copper	0·09515	31·7	3·0162
Lead	0·03140	103·6	3·2530
Mercury (solid)	0·03192	100	3·192
" (liquid)	0·03332	"	3·332
Platinum	0·03243	98·6	3·1976
Palladium	0·05927	53·2	3·1531
Rhodium	0·05408	52·2	2·8229
Osmium	0·03063	99·4	3·0446
Phosphorus	0·1887	31	5·8497
Iodine	0·05412	127	6·8732
Bromine (solid)	0·0843	80	6·744
Bromine (liquid)	0·106	"	8·48
Potassium	0·6956	39	6·712
Sodium	0·2934	23	6·748
Antimony	0·05077	120	6·0924
Arsenic	0·08140	75	6·1050
Bismuth	0·03084	213	6·5689
Silver	0·05701	108	6·1570
Gold	0·03244	196·6	6·3777

(1477) *Atomic Heats of Compound Bodies.*—The alloys according to Regnault's experiments, yield a specific heat which is exactly the mean of that of their components; hence their atomic heat is equal to the sum of those of their components: but with this exception, the atomic heat of a compound body cannot be calculated like its chemical equivalent, from the sum of the atomic heats of its constituents. The atomic heat of the compound is very generally less than that sum, and it varies from this number according as, during combination, condensation of the component particles has occurred to a greater or less extent, and according to other hitherto unascertained causes.

On comparing together equivalent quantities of isomorphous compounds possessed of a similar chemical composition, Neumann found that they likewise possessed equal atomic heats. The differences from the mean are in some cases considerable, but they are of the same order as those already observed to occur in the simple bodies. The mean atomic heat of the isomorphous carbonates, such, for example, as the carbonates of lime, baryta, iron, lead, zinc, strontia, and the double carbonates of lime and magnesia, is 10·61, varying between 10·55 and 10·85. In like manner the sulphates of baryta, lime, strontia, and lead, yield a mean atomic heat of 12·41, Regnault, from an extensive series of experiments on a great riety of compound bodies, has arrived at the conclusion that, [n all compound bodies of the same atomic composition, and of nilar chemical constitution, the specific heats are inversely as e atomic weights." The product obtained by multiplying the ecific heat into the equivalent number in any one class of comunds may, however, differ greatly from the product of the corsponding numbers in any other class, the numbers furnished by e different classes not being connected by any very simple ratio. iese facts will be rendered obvious by an examination of the subned summary of Regnault's results (*Ann. de Chimie*, III. i. 172).

Atomic Heats.

Class of Bodies.	General Formula.	Atomic Heat. (Sp. Heat × Eqt. No.)	Number of examples
Elements (1st class)		3·13	17
Do. (2nd do.)		6·39	10
Protoxides (1st class) (ZnO)	MO	4·99	2
Do. (2nd do.) (Pb O)	MO	5·76	5
Protosulphides	MS	6·20	7
Sesquioxides	M_2O_3	13·57	6
Sesquisulphides	M_2S_3	15·28	2
Binoxides	MO_2	6·92	3
Chlorides	MCl	9·36	8
Iodides . 1st class.	MI	9·67	2
Bromides . (such as BaCl)	MBr	9·68	1
Fluorides	MF	8·40	1
Chlorides	MCl	12·84	5
Iodides . 2nd class.	MI	13·40	5
Bromides . (such as NaCl)	MBr	13·70	3
Bichlorides	MCl_2	18·64	2
Terchlorides	MCl_3	30·22	2
Nitrates	MO, NO_5	24·13	3
Sulphates . . . 1st class.	MO, SO_3	13·28	5
Carbonates . . . (BaO, CO_2)	MO, CO_2	10·77	8
Sulphates . . . 2nd class.	MO, SO_3	16·54	2
Carbonates . . . (NaO, CO_2)	MO, CO_2	14·74	2

§ III. Atomic Relations of Heat of Combination.

(1478) *The quantity of Heat developed by Chemical Action is finite.*—Not only are the specific heats of the elements thus timately related to each other, but the amount of heat which ey emit when entering into combination is definite, and has a ecific relation to the combining number of each substance. hen the same substance is burned with a due supply of oxygen, d with suitable precautions, a given weight of it always emits the same amount of heat. Thus 1 lb. of hydrogen, when burned in oxygen, always emits heat enough to melt 315·2 lb. of ice; 31 lb. of phosphorus, when burnt to phosphoric acid, yields heat sufficient to melt 1576 lb. of ice; and 6 lb. of carbon when converted into carbonic acid, emits heat sufficient to melt 350 lb. of ice. It would at first sight appear easy to determine by direct experiment the amount of heat which each body emits in the act of combining with an equivalent of oxygen, and to compare the results thus obtained, with a corresponding series of experiments made by combining the same elements with chlorine. Independently, however, of the difficulties which the exact admeasurement of heat always involves, there are others which will be rendered evident by a little consideration.

Scarcely any molecular change can take place without either evolution or absorption of heat. When a gas or a vapour becomes liquified or solidified, the change of state is always attended by the evolution of the heat which it previously contained in a latent state (164), and the effect is reversed when a solid passes into the liquid or the aeriform condition, heat being then absorbed (162). Now, the instances in which chemical combination takes place without any alteration in the physical condition of bodies are rare, and the cases in which the product occupies exactly the same bulk as the bodies from which it was formed, are still more so. When two gaseous elements, like chlorine and hydrogen, unite and form a compound which is not only gaseous, but which occupies the same bulk as the bodies did before their combination, the problem is presented in the simplest form: the heat observed in such a case is due solely to the chemical action; but when the products, though gaseous, occupy a smaller bulk after they have entered into combination,—as when 2 volumes of carbonic oxide unite with 1 volume of oxygen, and form but 2 volumes of carbonic acid,—the heat emitted during the act of combination is due partly to chemical action, and partly also to the condensation which the gases have experienced. When the product assumes the liquid form, as occurs in the formation of water during the combustion of hydrogen in oxygen, the quantity of heat emitted owing to this change in form is still more considerable. When, on the other hand, a solid passes into the aeriform state, as when carbon is converted into carbonic acid, the heat actually observed is less than that which the combination ought really to produce: and the effect is reversed when the solid form is assumed by the product, as when phosphorus becomes oxidized to phosphoric acid;

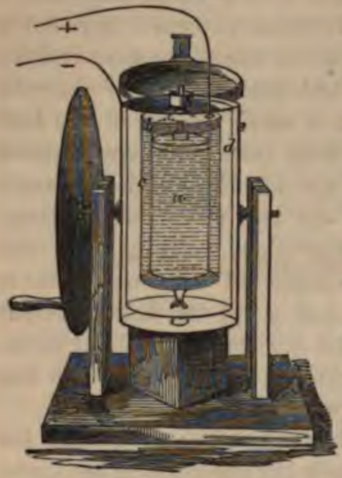
in which case the heat evolved exceeds that really due to the act of combination. But even when no change of state is observed, minor disturbing causes are at work. Supposing it were possible to obtain a direct combination of iodine with a metal, such as iron or zinc; even then, though two solids united to form a third solid, it would not necessarily happen that the whole of the heat emitted was due to the chemical action. If the iodide of zinc, for example, contracted in the act of combination, a small portion of the heat observed would be due to that evolved by the solid in consequence of its change of bulk; whereas, if the iodide occupied a larger space after combination than that of the two elements separately, the heat observed would be less than that resulting from the chemical action: and even if no change of bulk occurred, it might happen that the compound had a specific heat different from that of the original elements, and in such case a slight elevation or depression of temperature might be occasioned, which was not really the chemical result of the act of combination.

From the foregoing statements it is therefore clear that the experimental numbers, however carefully the observations are made, can very rarely yield the actual quantities of heat due to the chemical actions: they are compound results, from which the true *calorific equivalents* of the different elements (or heat evolved by the combination of chemical equivalents of the different elements), must be deduced by other means.

(1479) The importance of determining accurately the amount of heat arising from chemical action, was first distinctly announced by Lavoisier, who instituted a series of experiments with the view of finding the quantity of heat evolved during the combustion of various substances: his method consisted in ascertaining the quantity of ice which was melted, when given weights of these bodies were burned in his calorimeter. The first experiments with any claim to accuracy, however, are those of Dulong, which have formed the foundation for all subsequent researches upon the subject. Important additional investigations have since been made, particularly by Despretz, and recently by Andrews, and by Favre and Silbermann.

(1480) *Researches of Andrews.*—The apparatus employed by Andrews in these experiments (*Phil. Mag.*, May, 1848), was of a simple kind. When the substances to be combined were in the gaseous state, and the products of combustion were also gaseous, the two gases were mixed in the proper proportions, as in the performance of a eudiometric experiment, and introduced into a vessel of thin sheet copper (*a*, Fig. 338), of a capacity of about 24 cubic inches. It was closed by a screw, the head of which was perforated to admit a cork, through which a silver wire, *b*, passed, which was connected by a thin platinum wire within the vessel to a second silver wire soldered to the screw itself; this platinum wire could be ignited by connecting it for an instant with a small voltaic battery, and thus the gaseous mixture could be detonated at the pleasure of the operator. The copper vessel containing the mixed gases was then introduced into a larger vessel, *c*, which was filled up with water; the vessel, *c*, was suspended in a cylinder, *d*, provided with a moveable cover, and the whole was enclosed in an outer cylindrical vessel, *e*, arranged so as to admit of its being made to rotate upon its shorter axis.

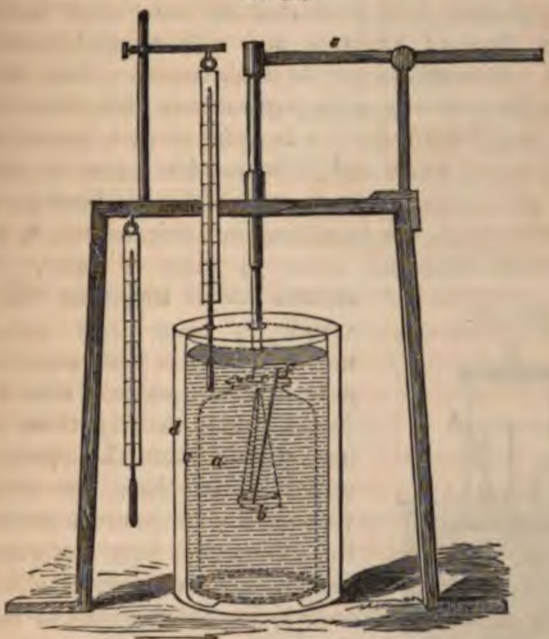
FIG. 338.



The apparatus having been mounted, was caused to rotate, in order to bring every part to a uniform temperature, and the exact amount of this initial temperature was then read off by a very sensitive thermometer, capable of indicating differences of temperature of $\frac{1}{500}$th of a degree Centigrade. The thermometer was then withdrawn, and the gases exploded by igniting the fine platinum wire; the outer vessel of water was closed by a cork, and the apparatus was caused to rotate for thirty-five seconds, in order to establish an equilibrium of temperature in all its parts. The thermometer was again introduced, and the rise of temperature was ascertained. After this observation the apparatus was again made to rotate for thirty-five seconds, and the loss of heat thus occasioned was ascertained. This third rotation was necessary in order to determine the cooling effect of the atmosphere upon the apparatus, during the time that the experiment lasted: in these cases it seldom amounted to more than $\frac{1}{400}$th of the total quantity of heat set free.

When solid bodies were burned in oxygen, the form of the apparatus was modified; the combustion was effected in a copper vessel (*a*, Fig. 339), of about 250 cubic inches in capacity, which was filled with oxygen; and a known weight of the combustible was supported in a small platinum dish, *b*; when all was ready, the vessel, *a*, having been accurately closed, the combustible was ignited by means of a voltaic current sent through a very fine platinum wire in connexion with the insulated wire, *f*. Previous to this ignition the vessel, *a*, was immersed in a large cylinder, *c*, filled with a known quantity of water, and the whole was surrounded by an outer vessel of tinplate, *d*, to prevent the effects of radiation. The copper vessel could be agitated within the vessel of water by means of the lever, *e*. Particular expedients were required in certain cases to ensure the ignition; thus, in burning zinc filings and other metals in oxygen, a minute portion of phosphorus was employed to kindle the metal; the weight of this piece of phosphorus being known, the heat which it emitted was calculated, and deducted from that observed. In some cases these experiments lasted fifteen or sixteen minutes, so that the correction for the cooling effect of the external air acquired considerable importance.

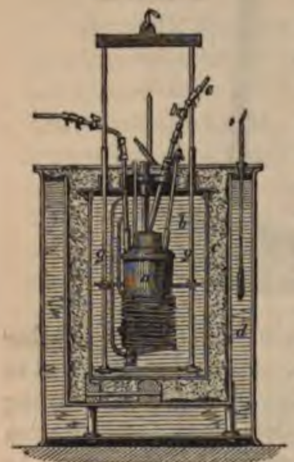
Fig. 339.



When chlorine was used instead of oxygen, it was not necessary to ignite the substance under trial; but in order to prevent the spontaneous ignition of the body, the latter was enclosed in a thin glass bulb, which was broken by agitation of the apparatus at the moment that everything was prepared. The chlorine itself was in most instances contained in a glass vessel, which was filled with the gas by displacement; an excess of the body for combination with the chlorine was always employed, so as to ensure the total absorption of the chlorine. The time allowed for absorption was in each case six minutes and a half.

(1481) *Experiments of Favre and Silbermann.*—A very extensive series of researches upon the development of heat during molecular and chemical changes was undertaken by Favre and Silbermann (*Ann. de Chimie*, III. xxxiv., xxxvi., and xxxvii). These experiments were conducted in many cases upon a larger scale than those of Andrews, and with a much more elaborate apparatus. It is satisfactory to find, however, that their experimental results generally agree pretty closely with those of Andrews, although they differ from him in some of their deductions. The essential part of Favre and Silbermann's apparatus was a vessel of brass gilt, *a*, Fig. 340, in which the combustions were performed; this vessel was immersed in a calorimeter, *b*, of silvered copper, which contained about 3½ pints of water. The calorimeter was supported in an outer vessel, *c*, lined with swan's down, and this case was itself surrounded by an outer double envelope, *d*, filled with water. It was found that by these means the loss of heat from the influence of the external atmosphere was reduced to a very small and measurable amount. When the combustions were performed in oxygen, this gas, previously dried, was allowed to flow into the combustion chamber by the tube, *e*, and the gases produced, together with the superfluous oxygen, were forced, previous to their exit from the apparatus, to traverse a spiral tube of thin copper, *f*, so that they might be completely cooled down to the temperature of the water in the calorimeter, *b*: *g g* is an agitator for ensuring uniformity of temperature in the water of the calorimeter.

Fig. 340.



Solid bodies were kindled by the introduction of small pieces of burning charcoal; liquids were burned in small lamps with asbestos wicks, and gases were introduced by a jet previously set on fire. The apparatus in the figure shows the arrangement for burning carbon; the scale of the thermometers employed allowed a variation of $\frac{1}{10}$th of 1°C. to be estimated. In most cases the weight of the substance burned was ascertained by collecting and weighing the products of combustion.

(1482) The following table is compiled chiefly from the results of Dulong, Andrews, and Favre and Silbermann. It is founded upon the direct results obtained by the rapid combustion, in oxygen, of the various substances enumerated in the first column. The *heat unit* adopted is the one proposed by Dulong, viz., the quantity of heat required to raise one gramme of water 1° C., or rather, from 0° C. to 1° C. The second column indicates the units of heat evolved during the act of combustion; or the weight in grammes of water which would be raised from 0° C. to 1° by the combustion of 1 gramme of each substance. The third column indicates the weight of water heated to the same amount by the combination of 1 gramme of oxygen with each body, and the fourth column (the *calorific equivalent*) is obtained by multiplying the numbers in the third column by 8 (the equivalent number of oxygen).

Heat developed during Combustion in Oxygen.

Substances burned.	Heat Units.		Calorific equivalent	Compound formed.	Observer.
	Grammes of water raised 1° C, by 1 gramme of each element.	Grammes of water raised 1°C by combination of 1 gramme of oxygen.	Grammes of water raised 1°C for 8 grammes (1 eqt.) of oxygen.		
Hydrogen	34462	4307	34462	HO	Favre and Silbermann.
„	33808	4226	33808	„	Andrews.
„	34743	4343	34743	„	Dulong.
Carbon	8080	3030	24240	CO_2	Favre and Silbermann.
„	7900	2962	23696	„	Andrews.
„	7912	2967	23736	„	Despretz.
Sulphur	2220	2220	17760	SO_2	Favre and Silbermann.
„	2307	2307	18456	„	Andrews.
„	2601	2601	20808	„	Dulong.
Phosphorus . . .	5747	4509	36072	PO_5	Andrews.
„ . . .	5669			„	Abria.
Zinc	1301	5285	42282	ZnO	Andrews.
„	1298	5273	42185	„	Dulong.
Iron	1576	4134	33072	Fe_3O_4	Andrews.
„	1702	4340	34720	„	Dulong.
Cobalt	1080	3995	31960	?	„
Nickel	1006	3723	29784	NiO	„
Tin	1233	4545	36360	SnO_2	„
„	1144	4230	33519	„	Andrews.
Antimony . . .	961	5875	47000	SbO_4	Dulong.
Copper	602	2394	19152	CuO	Andrews.
„	632	2512	20096	„	Dulong.

Heat developed during Combustion in Oxygen.

[*Continued.*]

Substances burned.	Heat units.		Calorific equivalent	Compound formed.	Observer.
	Grammes of water raised 1°C., by 1 gramme of each element.	Grammes of water raised 1° C., by combination of 1 gramme of oxygen.	Grammes of water raised 1° C., for 8 grammes (1 eqt.) of oxygen.		
Carbonic oxide .	2634	4609	36876	CO_2	Dulong.
" . .	2431	4258	34034	"	Andrews.
" . .	2403	4205	33642	"	Favre and Silbermann.
Protoxide of tin .	534	4473	35784	SnO_2	Dulong.
" .	521	4349	34792	"	Andrews.
Suboxide of copper	256	2288	18304	CuO	"
"	244	2185	17480	"	Dulong.
Cyanogen . . .	5195	4221	33768		"
Marsh gas . . .	13063	3266	26128		Favre and Silbermann.
" . . .	13185	3296	26368		Dulong.
" . . .	13108	3277	26216		Andrews.
Olefiant gas . . .	11942	3483	27864		"
" . . .	11858	3458	27664		Favre and Silbermann.
" . . .	12030	3514	28112		Dulong.
Alcohol	6909	3311	26488		"
"	6850	3282	26256		Andrews.
"	7183	3442	27536		Favre and Silbermann.
Ether	9027	3480	27840		" "
Olive oil	9862				Dulong.
Oil of turpentine .	10852	3294	26352		Favre and Silbermann.

The following tables contain the results of a similar series of experiments, in which chlorine, bromine, and iodine were employed instead of oxygen:—

Quantities of Heat disengaged by the Action of Chlorine.

Elements operated on.	Grammes of water raised 1° C., by combination of 1 gramme of substance.	Grammes of water raised 1° C., by combination of 1 gramme of chlorine.	Grammes of water raised 1° by combination of 1 eqt. (35·5 grammes) of chlorine.	Compound produced.	Observer.
Hydrogen .	24087	678	24087	HCl	Abria.
Hydrogen .	23783	670	23783	"	Favre & Silbermann.
Phosphorus	3422?	607	21548	PCl_5?	Andrews.
Potassium .	2655	2943	104476	KCl	"
Zinc . . .	1529	1427	50658	ZnCl	"
Iron . . .	1745	921	32695	Fe_2Cl_3	"
Tin . . .	1079	897	31722	$SnCl_2$	"
Antimony .	707	860	30401	$SbCl_3$	"
Arsenic . .	994	704	24992	$AsCl_3$	"
Copper . .	961	859	30494	CuCl	"
Mercury .	?	822	29181	?	"

Quantities of Heat disengaged by the Action of Bromine and Iodine.

Elements operated on.	Grammes of water raised 1° C., by combination of 1 gramme of substance.	Grammes of water raised 1° C., by combination of 1 gramme of chlorine.	Grammes of water raised 1° by combination of 1 equivalent (35·5 grammes) of chlorine.	Compound produced.	Observer.
		Bromine.			
Zinc . . .	1269	508	40640	ZnBr	Andrews.[*]
Iron . . .	1277	298	23833	Fe_2Br_3	„
		Iodine.			
Zinc . . .	819	209	26617	ZnI	„
Iron . . .	463	63	8046	Fe_2I_3	„

From an inspection of the preceding tables it may be gathered that the amount of heat disengaged by the following bodies, in their ordinary physical state, during their combination with an equal weight of oxygen is nearly the same: viz., hydrogen, carbonic oxide, cyanogen, iron, and tin, to which also may be added protoxide of tin, and phosphorus, though the heat disengaged by the body last named is somewhat higher than that furnished by any one of the others. If, however, to these numbers the corrections due to the change in the physical state of the products could be applied, the same coincidence would not be observed; but, although the trustworthy numerical data required for making these corrections do not exist, it is quite obvious that when equivalent quantities of the different elements unite with equal weights of oxygen without undergoing change in their physical state, they emit specific, but different amounts of heat. Sulphur, copper, and protoxide of copper, disengage little more than half the heat of the substances just mentioned, and carbon is intermediate between these two groups. Zinc gives out more heat than either, and potassium more than zinc.

(1483) *Influence of Dimorphism.*—According to the experiments of Favre and Silbermann, the same substance, when in different allotropic conditions, evolves somewhat different amounts of heat during combustion. The following results with carbon, and sulphur, in different states may be given in illustration of this point:

	Units of Heat.
Diamond evolves	7770
Graphite	7796
Wood Charcoal	8080
Octohedral Sulphur	2220
Prismatic	2264
Viscous Sulphur	2258.

---

[*] *Transactions of the Royal Irish Academy*, vol xix. 1843.

Similar differences were observed when different forms of the same compound body were submitted to experiment. According to these observers heat was evolved during the conversion of aragonite into calcspar; this is somewhat remarkable, for the density of calcspar is less than that of aragonite, and hence from analogy, an absorption of heat was rather to be looked for in this change.

(1484) *Heat evolved in certain cases during Decomposition.*—In the experiments of Dulong it appeared that when oxide of carbon, or hydrogen, was burned in protoxide of nitrogen, a larger amount of heat was evolved than when the same weights of these gases were burned in oxygen: following up this observation, Favre and Silbermann were led to the remarkable conclusion, that protoxide of nitrogen, in the act of decomposition, evolves a considerable amount of heat; and they estimate that not less than 1154 units of heat are evolved in the separation into its elements of a quantity of nitrous oxide which contains 1 gramme of oxygen. In the decomposition of peroxide of hydrogen also, heat is evolved instead of being absorbed, and they estimate the heat evolved during the liberation of 1 gramme of oxygen from peroxide of hydrogen at 1363 heat units.

Chemists are also familiar with other cases in which decomposition is attended with disengagement of heat; as when the oxides of chlorine, and the so-called iodide, and chloride, of nitrogen are decomposed. In these cases evolution of light and heat occurs, although the products of decomposition occupy a larger bulk than the compound which furnishes them. A still more striking evolution of heat attends the explosive decomposition of gun-cotton, although the gases produced occupy many hundred times the volume of the original substance. The latter case is particularly instructive, for it is obvious that the oxygen and carbon, although present in the compound, are each there in a form in which they retain a large share of heat, ready to be evolved when more intimate chemical union occurs.

(1485) *Combustion of Polymeric and Homologous Compounds.*—Favre and Silbermann have likewise examined the amount of heat developed during the combustion of many hydrocarbons, and compound ethers. From these experiments it appears that polymeric bodies do not emit equal amounts of heat during combustion; but that the denser the vapour which they furnish, the smaller is the amount of heat which they evolve in combining with equal weights of oxygen. The following table, which indicates the amount of heat given out by hydrocarbons polymeric with olefiant gas, distinctly shows this:—

		Heat Units.
Olefiant Gas . . .	C_4H_4 . . .	11858
Amylene	$C_{10}H_{10}$ . . .	11491
Paramylene . . .	$C_{20}H_{20}$ . . .	11303
Cetene	$C_{32}H_{32}$ . . .	11055
Metamylene . . .	$C_{40}H_{40}$ . . .	10928

In homologous compounds, such as the alcohols, and the fatty acids, it was also found that for equal weights of oxygen consumed, the heat of combustion was diminished, the oftener that the group of elements (C_2H_2) entered into the formation of the compound.

Even in metameric bodies, which contain the same number of equivalents, and which yield vapours of the same density, the quantity of heat evolved during combustion is not necessarily the same: from which it would appear that differences in the molecular arrangement of the component elements, although the number of the atoms may remain unaltered, may yet produce differences in the amount of heat evolved during oxidation. For example, the following metamerides evolve different quantities of heat:—

		Heat Units.
Propionic acid . . .	$HO, C_6H_5O_3$ . . .	4670
Formic ether . .	C_4H_5O, C_2HO_3 . . .	5279
Acetate of methyl .	$C_2H_3O, C_4H_3O_3$ . . .	5344

(1486) *Indirect Methods of Estimating Calorific Equivalents.*—The difficulties experienced in effecting the direct combustion of the metals in oxygen, chlorine, iodine, and sulphur, in such a manner as to ensure the perfect conversion of the metal into a given compound, unmixed with any other body of higher or lower degrees of oxidation, &c., are so considerable, that Favre and Silbermann were led to attempt the solution of this problem by indirect means. An examination of one of the methods employed in the case of the oxides, will furnish an idea of the general principle upon which they proceeded.

Whenever a metal is acted upon by an acid, or when one metal is employed to precipitate another metal from any of its salts, as when zinc is dissolved in sulphuric acid, or when copper is precipitated by means of zinc from a solution of its sulphate, heat is evolved. The calorific effects thus obtained are, however, complicated results; for several chemical processes concur in each operation, some of these processes being attended with the absorption, others with the evolution of heat. The calorimeter, of course, only measures the difference of these quantities.

Now, if it be assumed that the quantity of heat which is absorbed when a compound is separated into its elements is the same as that evolved in the formation of that compound, it becomes possible to calculate the value of the calorific action of any one particular chemical operation in the entire process, provided that the heat produced or absorbed in the other portions of the process be determined by other experiments. Suppose, for instance, we take the case of the solution of zinc in dilute sulphuric acid—the elevation of temperature observed will be the resultant of the following operations:—

In the first place, heat is evolved by the combination of an equivalent of zinc with one of oxygen. Let this amount of heat $=x$.

Secondly, heat is produced by the solution of the oxide of zinc in sulphuric acid: let this $= a$.

Thirdly, heat is absorbed by the separation of the oxygen and hydrogen during the decomposition of a quantity of water equivalent to that of the zinc dissolved: let this $= b$.

If T be the number of heat units indicated by the rise of temperature observed in the calorimeter, supposing a and b to be known from previous experiments, it is obvious that $x = \mathrm{T} - a + b$.

Experiment shows that T, the heat evolved during the solution of 1 gramme of zinc, is equal to 567·9 heat units. The solution in sulphuric acid of 1 gramme of zinc converted into oxide, gave for a a quantity equal to 335·54: and b, the heat absorbed during the decomposition of a quantity of water equivalent to a gramme of zinc, was equal to 1060·39 units, or

$$\frac{34462}{32{\cdot}5} \text{ or } \frac{\text{the calorific equivalent of hydrogen}}{\text{the chemical equivalent of zinc}} = 1060{\cdot}39$$

consequently, x, the heat attendant on the oxidation of zinc, is thus obtained:—

$$\begin{array}{rcr}
 & & \text{Heat Units.} \\
\mathrm{T} & = & 567{\cdot}90 \\
+\ b & = & 1060{\cdot}39 \\
\hline
 & & 1628{\cdot}29 \\
-\ a & = & 335{\cdot}54 \\
\hline
x & = & 1292{\cdot}75 \\
\hline
\end{array}$$

This number agrees very closely with the direct determination by Andrews and by Dulong, both of whom burned the metal in oxygen. The experiments of Andrews would give the number 1301, and those of Dulong 1298. But although the results agree very well in the present instance, the divergences are much greater in the case of iron and of copper.

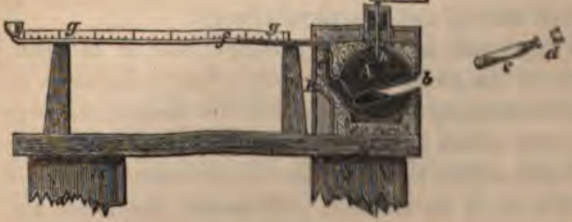
The following are the results deduced by Favre and Silbermann, by operations conducted upon this principle; the quantities of heat evolved being calculated for 1 gramme of each element, when combined with a single equivalent of the bodies with which it is united:—

	Oxides.	Chlorides.	Bromides.	Iodides.	Sulphides.
Hydrogen .	34462	23783	9322	—3606	2741
Potassium .		2587·7	2308	1977·2	1170·8
Sodium . .		4125·9			
Zinc . . .	1291	1547·5			644·3
Iron . . .	1352·6	1775·5			634·0
Copper . .	683·9	922·7			285·4
Lead . . .	266·1	430·1	315·4	223·1	91·9
Silver . .	56·6	322·2	237·2	172·7	51·1

Notwithstanding the confidence with which these numbers are put forward by their authors, it must be admitted that the data necessary for the calculations by which they were obtained are as yet very incomplete. The latent heat of oxygen in the gaseous state is unknown, and other important numbers are wanting; the results given in the foregoing table cannot, therefore, at present be received without great reserve.

(1487) *Mercurial Calorimeter of Favre and Silbermann.*—Most of these experiments were performed by the aid of a *mercury calorimeter* (*Ann. de Chimie,* III. xxxvi. 33). This instrument may be regarded as a mercurial thermometer, with a very large bulb capable of receiving within it the substances which were submitted

FIG. 341.



to experiment. It consists of a large glass globe, A, Fig. 341, of the capacity of about 32 fluid ounces, provided with three apertures, one at the top and two at the sides. Into one of the lateral apertures, *b*, is fixed obliquely a tube of thin iron or platinum, closed at the bottom; and into this tube, which is called the *muffle*, is introduced another tube, *c*, of very thin glass, containing the substances which are to be submitted to experiment: this glass tube is fitted into the metallic tube by means of a cork, *d*; a small quantity of mercury is placed within the muffle, the object of this expedient being to transmit the heat rapidly from the glass tube to the body of the calorimeter. The second lateral aperture, *c*, terminates in a neck which is curved vertically upwards, and into which is cemented the bent extremity of a horizontal capillary tube, *f*, of uniform bore, open at both ends, and 18 or 20 inches in length: by means of this tube the changes in volume of the mercury can be measured upon the scale, *g g*. Through the upper aperture of the globe passes a steel piston, *h*, moved by a screw, by which means the column of mercury in the capillary tube can be reduced at pleasure to the zero of the scale. The globe is itself enclosed in a wooden case, *k*, lined with swan's-down in order to diminish the disturbing effects of external changes of temperature.

The value of the amount of expansion indicated was at once transformed into *units of heat*, by ascertaining the amount of expansion produced by the cooling of a given weight of water from the boiling point, to a measured degree of temperature: by multiplying the weight of water in grammes by the number of degrees Centigrade which it had lost in cooling, the number of *units of heat* was ascertained; since, by our definition, a unit of heat is the quantity of heat required to raise 1 gramme of water 1° C. The number of inches by which the mercurial column had advanced in the capillary tube during the operation was next accurately measured; and by dividing this measured column by the number of heat units, the instrument was graduated so as to enable the observer to record at once the number of units of heat disengaged or absorbed during any chemical change.

This apparatus is good in principle, but it is open to certain objections in the mode of its construction:—the sides of the glass vessel are necessarily thick, to enable it to sustain the large weight of mercury with which it is filled; the glass, therefore, cannot rapidly and certainly adjust itself to the temperature of the hot mercury with which it is in contact. Moreover the tubes are cemented into the three openings with mastic or marine glue. The apparatus, to work well, should have been filled like a barometer or thermometer, since the presence even of a small bubble of air would materially affect the accuracy of the results. It is true that it is stated that the globe was filled with mercury *in vacuo*, but with cemented joints this precaution would soon be rendered useless. It is therefore necessary in estimating the amount of confidence due to the results obtained by its use, to bear in mind these possible sources of inaccuracy. This is the more necessary, since it is principally in the results obtained by the use of this apparatus that the results of Favre and Silbermann differ from those of Andrews. At the same time it is to be remarked, that the results published by the French observers appear to be very consistent with each other.

(1488) *On the Heat evolved during Metallic Precipitations.*—On the other hand it must be stated that the varied and careful experiments of Andrews (*Phil. Trans.* 1848) upon the heat evolved during the precipitation of several metals from their salts by the action of other metals, furnished numerical results differing from those calculated by Favre and Silbermann. In the experiments of Andrews, the corrections required are not in all cases completely under exact experimental control; in the displacement of copper by lead the correction amounts to one-eighth of the whole increment of heat, but in other instances the correction is trifling, not exceeding one-fiftieth of the amount of heat evolved; the results obtained are mutually consistent. An additional test of the accuracy of this method is afforded by the results furnished in two different series of experiments by the amount of heat obtained during the precipitation of copper by zinc, the corresponding numbers in both sets of experiments agreeing very closely with each other. In the first set of experiments a strong solution of sulphate of copper was precipitated with zinc in a small glass vessel, and the heat estimated by the rise of temperature experienced by the water of a calorimeter in which the glass vessel was contained: in the second series, a dilute solution of sulphate of copper was employed, and the heat was measured by the rise of temperature experienced by the liquid itself. The mean of 4 experiments by the first plan gave 864, as the number of units of heat evolved by the precipitation of each gramme of copper from its sulphate; whilst the mean of 5 experiments upon the latter method was 868.

The following are the numbers given by Andrews, but he has purposely abstained from any attempt to deduce from them the amount of heat developed during the indirect oxidation of the metal which acts as the precipitant:—

Table of Heat evolved during Metallic Precipitations.

Class of Salts used, and Metals employed for precipitating them.	Name of precipitated metal.	Units of heat evolved by precipitated metal.		Name of precipitating metal.	Units of heat for 1 gramme of precipitating metal.
		For 1 gramme.	For 1 equivalent.		
Salts of Copper by Zinc . .	Copper	866	27452	Zinc	847
Salts of Copper by Iron . .	Copper	592	18736	Iron	677
Salts of Copper by Lead .	Copper	268	8488	Lead	82
Salts of Silver by Zinc . .	Silver	426	45976	Zinc	1420
Salts of Silver by Copper .	Silver	161	17408	Copper	549
Salts of Lead by Zinc . .	Lead	182	18856	Zinc	585
Salts of Mercury by Zinc .	Mercury	333	33328	Zinc	1034
Salts of Platinum by Zinc .	Platinum	899	88680	Zinc	2750

In these experiments a known weight of finely divided zinc, iron, lead, or copper, as the case might require, was mixed with a solution of the salt to be decomposed; taking care that the metal employed was always more than sufficient completely to decompose the salt in solution: the rise of temperature which occurred was noted with the usual precautions.

Andrews states as the result of a large number of experiments, that the quantity of heat developed during the mutual action of the same pair of metals is the same, when an equivalent of one metal, A, displaces another metal, B, from any of its salts, whatever may be the acid of the salt employed, provided that B is in the same state of oxidation in each of the compounds submitted to experiment. But if a different metal be employed to effect the precipitation, the amount of heat evolved is different. Thus, whether chloride, or sulphate, or acetate, or formiate of copper be precipitated by zinc, the quantity of heat developed in each case for every equivalent of copper is sensibly the same, viz., 27452. But if iron be substituted for zinc in the precipitation of the copper, the amount of heat is different, viz., 18736; though iron evolves the same amount of heat, whether the sulphate or the chloride of copper be employed. The same principle has since been assumed by Favre and Silbermann in their calculations. If the metals be arranged in a list, beginning with those which emit the largest amount of heat when used as precipitants, the order in which they will stand is the following—zinc, iron, lead, copper, mercury, silver, and platinum. Now, it will be remarked that this is exactly in the electro-chemical order, zinc being the most electro-positive, and platinum the most electro-negative. Another interesting point of connexion between the thermal and the electrical phenomena exhibited by the metals, is to be observed in the fact that the nature of the acid contained in the salt which is undergoing decomposition, does not influence either its thermal equivalent, or the electro-motive force (228), which it exerts when employed in the production of voltaic action.

Another remarkable conclusion has been deduced by Andrews from these experiments:—If three metals, A, B, and C, be so related that A is capable of displacing B and C from their combinations, and B be also capable of displacing C, the heat developed by the substitution of A for C will be exactly equal to that developed in the substitution of A for B, together with that developed in the substitution of B for C:—

Heat Units.
Thus, 1 equivalent of lead displaced by zinc = 18856
1 equivalent of copper by lead . . = 8488

1 equivalent of copper by zinc . . = 27344

The experimental number being 27452

An analogous phenomenon is observed in the electrical relations of the metals (228): when three metals such as platinum, zinc, and potassium are arranged two and two in their electrical order, the electro-motive force generated between the two extremes, platinum and potassium, is equal to the sum of the electro-motive forces of the pairs platinum and zinc, and zinc and potassium.

(1489) *Calorific Equivalents of the Elements.*—The results obtained by the direct action of oxygen, chlorine, iodine and bromine upon various elementary bodies, are summed up in the following table, in which the numbers given indicate the quantity of heat evolved by the union of equivalent quantities of oxygen, chlorine, iodine, and bromine, with each element, taking as the standard of comparison, the number of grammes of water at 0° C., which would be raised to 1° C., by the combustion of 1 gramme of hydrogen in oxygen. The quantities of heat thus given out are termed by Favre and Silbermann, the *calorific equivalents* of the different elements.

The numbers to which an A is prefixed are those of Andrews; F. S. indicate those of Favre and Silbermann: when an asterisk is prefixed to any number, the result has been calculated by indirect methods, upon the principle already explained:—

Calorific Equivalents of various Elements.

Elements.		Oxygen.	Chlorine.	Bromine.	Iodine.	Sulphur.
Hydrogen . .	F.S.	34462	23783	*9322	*−3606	*2741
Carbon . . .	,,	24240				
Sulphur . .	,,	17760				
Phosphorus .	A.	36072				
Potassium . .	A.		104476			
Ditto . . .	F.S.		*100960	*90188	*77268	*45638
Sodium . . .	,,		94847			
Zinc	A.	42282	50658	40640	26617	
Ditto . . .	F.S.	*42451	*50296			*20940
Iron	A.	33072	32695	23833	8046	
Ditto . . .	F.S.	*37828	*49651			*17753
Tin	A.	33519	31722			
Arsenic . .			24992			
Antimony . .	Dulong	47000	A. 30401			
Copper . . .	,,	19152	30404			
Ditto . . .	F.S.	*21885	*29524			*9133
Lead . . .	,,	*27675	*44730	*32802	*23208	*9556
Silver . . .	,,	*6113	*34800	*25618	*18651	*5524

From an examination of this table, it will be obvious that the temperature evolved in the act of combination rises highest in those cases in which the chemical affinity between the two elements is the strongest, and where the compound possesses the greatest stability. No definite quantitative expression of the law which regulates the evolution of heat during combination, can, however, be deduced from these numbers, owing to the variety of disturbing causes (1478) when bodies are compared in the solid state.

(1490) *On the Heat developed during the Combination of Acids*

Heat Units evolved by the combination of 1 *Equivalent o*

	ANDREWS.									FAVRE	
Acids.	Potash.	Soda.	Baryta.	Ammonia.	Magnesia.	Lime.	Zinc.	Lead.	Silver.	Potash.	Soda.
Sulphuric .	15900	16200	...	13900	18500	...	11800	...	...	16083	15810
Sulphurous .	15900	...	...	...	...	...	...	...	...	...	...
Nitric. . .	14600	14000	14700	12200	17700	15700	10300	8900	6900	15510	15283
Phosphoric .	14200	14000	...	...	...	15500	...	...	...	17766	...
Arsenic . .	14100	13900	...	12200	...	...	...	...	...	...	...
Hydrochloric	14300	14700	14700	12200	17700	...	10600	...	...	15656	15128
Hydrobromic	...	...	...	...	...	...	...	...	...	15510	15159
Hydriodic .	14200	14100	14700	11900	...	...	9800	...	...	15698	15097
Chromic . .	14000	...	...	...	...	...	...	...	...	...	...
Oxalic . .	14400	14600	...	12400	...	...	...	...	...	14156	13752
Acetic . .	13800	13800	13700	11900	...	15300	...	8100	...	13973	13600
Formic . .	13900	...	...	..	...	...	...	...	...	...	13308
Tartaric . .	13200	12900	...	11200	...	...	...	...	...	13425	12651
Citric . .	13200	12900	...	11000	...	...	...	...	...	13658	13178
Succinic . .	13400	12900	...	11200	...	...	...	...	...		

with Bases.—A careful and extensive series of experiments upon the heat developed during the saturation of dilute solutions of different acids, by each of the more important bases with which they form soluble compounds, was published by Andrews in 1841. (*Trans. Roy. Irish Acad.*, vol. xix. Part II.) In these experiments, a slight excess of acid was purposely employed; the bases, where it was possible, being in a state of solution. When they were in the insoluble form, the heat observed was of course lower than that due to the chemical action; a portion being absorbed in the passage of the base from the solid to the liquid condition; but although the quantity of heat so absorbed is unknown, this amount would be constant for the same base, and therefore the observed results obtained for the combination of equal weights of this base with different acids would be mutually comparable. A *resumé* of this subject is given by the same author in a "Report on the Heat of Combination," published in the *Report of the British Association* for 1849, p. 69. From these experiments it appears:—

1. "That an equivalent of the same base, combined with different acids, produces *nearly* the same quantity of heat.

2. "An equivalent of the same acid, combined with different bases, produces different amounts of heat.

3. "When a neutral salt is converted into an acid salt by combining with one or more equivalents of an acid, no disengagement of heat occurs.

4. "When a double salt is formed by the union of two neutral salts, no disengagement of heat occurs.

the undermentioned Bases with 1 Equivalent of certain Acids.

AND SILBERMANN.

Baryta.	Ammonia.	Magnesia.	Lime.	Zinc.	Manganese.	Nickel.	Cobalt.	Iron protox.	Cadmium.	Copper.	Lead.	Silver.
...	14690	14440	...	10455	12075	11932	11780	10872	10240	7720	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...
15360	13676	12840	16943	8323	10850	10450	9956	9648	8116	6400	9240	6206
...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...
...	13536	13220	...	8307	11235	10412	10374	9828	8109	6416	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...
...	12649	12270	...	7720	9982	9245	9272	8590	7546	5264	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...
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...	...	...	...	...	...	...	...	...	...	...	...	...

5. "When a neutral salt is converted into a basic salt, the combination is accompanied by the disengagement of heat.

6. "When one and the same base displaces another from any of its neutral combinations, the heat evolved or absorbed, is always [nearly] the same, whatever the acid element may be."*

The results of Favre and Silbermann lead substantially to similar conclusions, though the absolute quantities of heat which they obtained in many cases, differ considerably from those given by Andrews. The table which is given on the preceding page indicates the amount of heat obtained by both observers by combining 1 equivalent of each of the different bases, with each acid, the acid being always very slightly in excess.

In the present stage of our knowledge upon this subject, it appears safest to state, that the quantity of heat emitted during the act of combination of equivalent quantities of different acids with a given base, although nearly the same, is not rigidly so. They might probably be arranged in *isothermic* groups, as follows, —those which stand first evolving most heat:—

	With 1 Eqt. of Potash.
1. Sulphuric and sulphurous acids	15900
2. Oxalic, nitric, phosphoric, arsenic, hydrochloric, hydriodic	14600—14200
3. Chromic, formic, acetic	14000—13800
4. Tartaric, citric, succinic	13200

The bases also differ in the amounts of heat which they emit in combining with the same acid, but as only a very few of the bases are soluble in water, their thermic powers cannot be compared in so simple a manner as those of the acids. Potash, soda, and baryta seem to be nearly isothermic, whilst ammonia is decidedly inferior to these bases. Lime, magnesia, and the other insoluble oxides cannot be satisfactorily compared with each other, until the amount of heat which is absorbed during their passage into the liquid form is known.

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* The author cannot here omit acknowledging the kindness of his friend Dr. Andrews, who has furnished him with a table of his experimental results, reduced from the paper in the *Transactions of the Royal Irish Academy* to the hydrogen unit, corrected for the specific heat of the solutions employed; this correction is very trifling in amount, but it was omitted, as stated, in the original paper. Dr. Andrews has also communicated to the author the result of an unpublished series of experiments just completed upon this subject, which were undertaken with a view of throwing light upon the difference between the conclusions arrived at by the French chemists, and those formerly published by the Professor of Belfast. The general result of these new experiments, which were performed with thermometers of greater delicacy than on the former occasion, and with additional precautions to avoid error, confirms the conclusions previously arrived at by Dr. Andrews.

APPENDIX.

Specific Gravities corresponding to Degrees of Baumé's Hydrometer for Liquids heavier than Water.

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
0	1·000	20	1·152	40	1·357	60	1·652
1	1·007	21	1·160	41	1·369	61	1·670
2	1·013	22	1·169	42	1·381	62	1·689
3	1·020	23	1·178	43	1·395	63	1·708
4	1·027	24	1·188	44	1·407	64	1·727
5	1·034	25	1·197	45	1·420	65	1·747
6	1·041	26	1·206	46	1·434	66	1·767
7	1·048	27	1·216	47	1·448	67	1·788
8	1·056	28	1·225	48	1·462	68	1·809
9	1·063	29	1·235	49	1·476	69	1·831
10	1·070	30	1·245	50	1·490	70	1·854
11	1·078	31	1·256	51	1·495	71	1·877
12	1·085	32	1·267	52	1·520	72	1·900
13	1·094	33	1·277	53	1·535	73	1·924
14	1·101	34	1·288	54	1·551	74	1·949
15	1·109	35	1·299	55	1·567	75	1·974
16	1·118	36	1·310	56	1·583	76	2·000
17	1·126	37	1·321	57	1·600		
18	1·134	38	1·333	58	1·617		
19	1·143	39	1·345	59	1·634		

Specific Gravities on Baumé's Scale for Liquids lighter than Water.

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
10	1·000	23	0·918	36	0·849	49	0·789
11	0·993	24	0·913	37	0·844	50	0·785
12	0·986	25	0·907	38	0·839	51	0·781
13	0·980	26	0·901	39	0·834	52	0·777
14	0·973	27	0·896	40	0·830	53	0·773
15	0·967	28	0·890	41	0·825	54	0·768
16	0·960	29	0·885	42	0·820	55	0·764
17	0·954	30	0·880	43	0·816	56	0·760
18	0·948	31	0·874	44	0·811	57	0·757
19	0·942	32	0·869	45	0·807	58	0·753
20	0·936	33	0·864	46	0·802	59	0·749
21	0·930	34	0·859	47	0·798	60	0·745
22	0·924	35	0·854	48	0·794		

The degrees of Twaddell's hydrometer are readily converted into their corresponding specific gravities by multiplying them by 5, and adding 1000. The following is a short table of

Degrees on Twaddell's Hydrometer, and the corresponding Specific Gravities.

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
1	1·005	8	1·040	15	1·075	22	1·110
2	1·010	9	1·045	16	1·080	23	1·115
3	1·015	10	1·050	17	1·085	24	1·120
4	1·020	11	1·055	18	1·090	25	1·125
5	1·025	12	1·060	19	1·095	26	1·130
6	1·030	13	1·065	20	1·100	27	1·135
7	1·035	14	1·070	21	1·105	28	1·140

English Weights and Measures.—Avoirdupois.

	Grains.	Drachms.	Ounces.	lb.	Qrs.	Cwt.	Tons.
Grain . .	1						
Drachm .	27·34	1					
Ounce . .	437·5	16	1				
Pound . .	7000	256	16	1			
Quarter .	196000	7168	448	28	1		
Cwt . . .	784000	28672	1792	112	4	1	
Ton . . .	15680000	573440	35840	2240	80	20	1

Troy Weight.

	Grains.	dwts.	Ounces.	lb.
Grain	1			
Pennyweight . .	24	1		
Ounce	480	20	1	
Pound	5760	240	12	1

1 cubic inch of distilled water in air at 62° F. = 252·456 grains.
1 cubic inch of distilled water *in vacuo* at 62° F. = 252·722 grains.

Cubic Inches.
1 Gallon = 277·276
1 Pint = 34·659
1 Fluidounce = 1·7329
1 Litre = 61·024
1 Cubic centimetre = 0·061024

1 Cubic inch = 16·387 cubic centimetres.

1·00000 parts of gas at 32° F., 29·922 Bar. (also at 32°), become at 60° F., Bar. 30 inches (also at 60°) = 1·05720 parts.

Comparison of French and English Weights.

		Grains.			Grains.
1 Gramme	=	15·432348	6 Grammes	=	92·594088
2 ,,	=	30·864696	7 ,,	=	108·026436
3 ,,	=	46·297044	8 ,,	=	123·458784
4 ,,	=	61·729392	9 ,,	=	138·891132
5 ,,	=	77·161740	10 ,,	=	154·323480

The weight of a gramme is that of a cubic centimetre of distilled water at 39°·2 F.

		Grains.		oz. Av.		lb. Av.
1 **Milligramme**	=	0·01543				
1 **Centigramme**	=	0·15432				
1 **Decigramme**	=	1·5432				
1 **Gramme**	=	15·432				
1 **Kilogramme**	=	15432·348	=	35·2739	=	2·2046

Comparison of French and English Measures.

		English Inches.		Feet.		Yards.
1 **Millimetre**	=	0·03937079				
1 **Centimetre**	=	0·3937079				
1 **Decimetre**	=	3·937079				
1 **Metre***	=	39·37079	=	3·280899	=	1·093633
1 **Kilometre**	=	39370·79	=	3280·899	=	1093·633

The length of the platinum metre is estimated at the temperature of 32° F., the English standard yard at 62° F.

		Fluid ounces.		Pints.
1 Litre	=	35·2754	=	1·76377

The capacity of a litre is that of a cube of a decimetre in the side.

To Reduce Grammes to Grains.

Log. Grammes + 1·188432 = log. Grains.

To Reduce Cubic Centimetres to Cubic Inches.

Log. cubic centimetres + (—2·7855007) = log. Cubic inches.

To Reduce Millimetres to Inches.

Log. millimetres + (—2·5951663) = log. inches.

To Convert Grains into Grammes.

Log. grains + (—2·8115680) = log. grammes.

To Convert Cubic Inches into Cubic Centimetres.

Log. cubic inches + 1·2144993 = log. cubic centimetres.

To Convert Inches into Millimetres.

Log. inches + 1·4048337 = log. millimetres.

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* The metre is a ten-millionth part of a quadrant of a meridian circle of the earth.

Values of Millimetres in English Inches.

Milli-metres.	English inches.	Milli-metres.	English inches.	Milli-metres.	English inches.
1	0·03937079	45	1·7716	125	4·941
2	0·07874158	50	1·968	130	5·118
3	0·11811237	55	2·165	135	5·315
4	0·15748316	60	2·362	140	5·512
5	0·19685395	65	2·559	145	5·708
6	0·23622474	70	2·756	150	5·906
7	0·27559553	75	2·953	155	6·103
8	0·31496632	80	3·149	160	6·299
9	0·35433711	85	3·346	165	6·496
10	0·39370790	90	3·543	170	6·693
15	0·5905	95	3·740	175	6·890
20	0·7874	100	3·937	180	7·087
25	0·9842	105	4·134	185	7·284
30	1·1811	110	4·331	190	7·480
35	1·3779	115	4·528	195	7·677
40	1·5748	120	4·744	200	7·874

Table of the corresponding Heights of the Barometer in Millimetres and English Inches.

Milli-metres.		English inches.	Milli-metres.		English inches.	Milli-metres.		English inches.
720	=	28·347	739	=	29·095	758	=	29·843
721	=	28·386	740	=	29·134	759	=	29·882
722	=	28·425	741	=	29·174	760	=	29·922
723	=	28·465	742	=	29·213	761	=	29·961
724	=	28·504	743	=	29·252	762	=	30·000
725	=	28·543	744	=	29·292	763	=	30·039
726	=	28·583	745	=	29·331	764	=	30·079
727	=	28·622	746	=	29·370	765	=	30·118
728	=	28·662	747	=	29·410	766	=	30·158
729	=	28·701	748	=	29·449	767	=	30·197
730	=	28·740	749	=	29·488	768	=	30·236
731	=	28·780	750	=	29·528	769	=	30·276
732	=	28.819	751	=	29·567	770	=	30·315
733	=	28·858	752	=	29·606	771	=	30·355
734	=	28·898	753	=	29·645	772	=	30·394
735	=	28·937	754	=	29·685	773	=	30·433
736	=	28·976	755	=	29·724	774	=	30·473
737	=	29·016	756	=	29·764	775	=	30·512
738	=	29·055	757	=	29·803			

Table for the Conversion of Degrees on the Centigrade Thermometer into those of Fahrenheit's Scale.

° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.
—100	— 148·0	— 49	— 56·2	2	35·6	53	127·4
— 99	— 146·2	— 48	— 54·4	3	37·4	54	129·2
— 98	— 144·4	— 47	— 52·6	4	39·2	55	131·0
— 97	— 142·6	— 46	— 50·8	5	41·0	56	132·8
— 96	— 140·8	— 45	— 49·0	6	42·8	57	134·6
— 95	— 139·0	— 44	— 47·2	7	44·6	58	136·4
— 94	— 137·2	— 43	— 45·4	8	46·4	59	138·2
— 93	— 135·4	— 42	— 43·6	9	48·2	60	140·0
— 92	— 133·6	— 41	— 41·8	10	50·0	61	141·8
— 91	— 131·8	— 40	— 40·0	11	51·8	62	143·6
— 90	— 130·0	— 39	— 38·2	12	53·6	63	145·4
— 89	— 128·2	— 38	— 36·4	13	55·4	64	147·2
— 88	— 126·4	— 37	— 34·6	14	57·2	65	149·0
— 87	— 124·6	— 36	— 32·8	15	59·0	66	150·8
— 86	— 122·8	— 35	— 31·0	16	60·8	67	152·6
— 85	— 121·0	— 34	— 29·2	17	62·6	68	154·4
— 84	— 119·2	— 33	— 27·4	18	64·4	69	156·2
— 83	— 117·4	— 32	— 25·6	19	66·2	70	158·0
— 82	— 115·6	— 31	— 23·8	20	68·0	71	159·8
— 81	— 113·8	— 30	— 22·0	21	69·8	72	161·6
— 80	— 112·0	— 29	— 20·2	22	71·6	73	163·4
— 79	— 110·2	— 28	— 18·4	23	73·4	74	165·2
— 78	— 108·4	— 27	— 16·6	24	75·2	75	167·0
— 77	— 106·6	— 26	— 14·8	25	77·0	76	168·8
— 76	— 104·8	— 25	— 13·0	26	78·8	77	170·6
— 75	— 103·0	— 24	— 11·2	27	80·6	78	172·4
— 74	— 101·2	— 23	— 9·4	28	82·4	79	174·2
— 73	— 99·4	— 22	— 7·6	29	84·2	80	176·0
— 72	— 97·6	— 21	— 5·8	30	86·0	81	177·8
— 71	— 95·8	— 20	— 4·0	31	87·8	82	179·6
— 70	— 94·0	— 19	— 2·2	32	89·6	83	181·4
— 69	— 92·2	— 18	— 0·4	33	91·4	84	183·2
— 68	— 90·4	— 17	+ 1·4	34	93·2	85	185·0
— 67	— 88·6	— 16	3·2	35	95·0	86	186·8
— 66	— 86·8	— 15	5·0	36	96·8	87	188·6
— 65	— 85·0	— 14	6·8	37	98·6	88	190·4
— 64	— 83·2	— 13	8·6	38	100·4	89	192·2
— 63	— 81·4	— 12	10·4	39	102·2	90	194·0
— 62	— 79·6	— 11	12·2	40	104·0	91	195·8
— 61	— 77·8	— 10	14·0	41	105·8	92	197·6
— 60	— 76·0	— 9	15·8	42	107·6	93	199·4
— 59	— 74·2	— 8	17·6	43	109·4	94	201·2
— 58	— 72·4	— 7	19·4	44	111·2	95	203·0
— 57	— 70·6	— 6	21·2	45	113·0	96	204·8
— 56	— 68·8	— 5	23·0	46	114·8	97	206·6
— 55	— 67·0	— 4	24·8	47	116·6	98	208·4
— 54	— 65·2	— 3	26·6	48	118·4	99	210·2
— 53	— 63·4	— 2	28·4	49	120·2	100	212·0
— 52	— 61·6	— 1	30·2	50	122·0	101	213·8
— 51	— 59·8	0	32·0	51	123·8	102	215·6
— 50	— 58·0	+ 1	33·8	52	125·6	103	217·4

Conversion of Degrees on the Centigrade Thermometer into those of Fahrenheit's Scale.

[*Continued.*]

° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.
104	219.2	155	311·0	206	402·8	257	494·6
105	221·0	156	312·8	207	404·6	258	496·4
106	222·8	157	314·6	208	406·4	259	498·2
107	224·6	158	316·4	209	408·2	260	500·0
108	226·4	159	318·2	210	410·0	261	501·8
109	228·2	160	320·0	211	411·8	262	503·6
110	230·0	161	321·8	212	413·6	263	505·4
111	231·8	162	323·6	213	415·4	264	507·2
112	233·6	163	325·4	214	417·2	265	509·0
113	235·4	164	327·2	215	419·0	266	510·8
114	237·2	165	329·0	216	420·8	267	512·6
115	239·0	166	330·8	217	422·6	268	514·4
116	240·8	167	332·6	218	424·4	269	516·2
117	242·6	168	334·4	219	426·2	270	518·0
118	244·4	169	336·2	220	428·0	271	519·8
119	246·2	170	338·0	221	429·8	272	521·6
120	248·0	171	339·8	222	431·6	273	523·4
121	249·8	172	341·6	223	433·4	274	525·2
122	251·6	173	343·4	224	435·2	275	527·0
123	253·4	174	345·2	225	437·0	276	528·8
124	255·2	175	347·0	226	438·8	277	530·6
125	257·0	176	348·8	227	440·6	278	532·4
126	258·8	177	350·6	228	442·4	279	534·2
127	260·6	178	352·4	229	444·2	280	536·0
128	262·4	179	354·2	230	446·0	281	537·8
129	264·2	180	356·0	231	447·8	282	539·6
130	266·0	181	357·8	232	449·6	283	541·4
131	267·8	182	359·6	233	451·4	284	543·2
132	269·6	183	361·4	234	453·2	285	545·0
133	271·4	184	363·2	235	455·0	286	546·8
134	273·2	185	365·0	236	456·8	287	548·6
135	275·0	186	366·8	237	458·6	288	550·4
136	276·8	187	368·6	238	460·4	289	552·2
137	278·6	188	370·4	239	462·2	290	554·0
138	280·4	189	372·2	240	464·0	291	555·8
139	282·2	190	374·0	241	465·8	292	557·6
140	284·0	191	375·8	242	467·6	293	559·4
141	285·8	192	377·6	243	469·4	294	561·2
142	287·6	193	379·4	244	471·2	295	563·0
143	289·4	194	381·2	245	473·0	296	564·8
144	291·2	195	383·0	246	474·8	297	566·6
145	293·0	196	384·8	247	476·6	298	568·4
146	294·8	197	386·6	248	478·4	299	570·2
147	296·6	198	388·4	249	480·2	300	572·0
148	298·4	199	390·2	250	482·0	301	573·8
149	300·2	200	392·0	251	483·8	302	575·6
150	302·0	201	393·8	252	485·6	303	577·4
151	303·8	202	395·6	253	487·4	304	579·2
152	305·6	203	397·4	254	489·2	305	581·0
153	307·4	204	399·2	255	491·0	306	582·8
154	309·2	205	401·0	256	492·8	307	584·6

Conversion of Degrees on the Centigrade Thermometer into those of Fahrenheit's Scale.

[*Continued.*]

° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.
308	586·4	330	626·0	351	663·8	480	896
309	588·2	331	627·8	352	665·6	490	914
310	590·0	332	629·6	353	667·4	500	932
311	591·8	333	631·4	354	669·2	600	1112
312	593·6	334	633·2	355	671·0	700	1292
313	595·4	335	635·0	356	672·8	800	1472
314	597·2	336	636·8	357	674·6	900	1652
315	599·0	337	638·6	358	676·4	1000	1832
316	600·8	338	640·4	359	678·2	1100	2012
317	602·6	339	642·2	360	680·0	1200	2192
318	604·4	340	644·0	370	698	1300	2372
319	606·2	341	645·8	380	716	1400	2552
320	608·0	342	647·6	390	734	1500	2732
321	609·8	343	649·4	400	752	1600	2912
322	611·6	344	651·2	410	770	1700	3092
323	613·4	345	653·0	420	788	1800	3272
324	615·2	346	654·8	430	806	1900	3452
325	617·0	347	656·6	440	824	2000	3632
326	618·8	348	658·4	450	842	2100	3812
327	620·6	349	660·2	460	860	2200	3992
328	622·4	350	662·0	470	878	2300	4172
329	624·2						

Quantities of Absolute Alcohol by Weight, in Mixtures of Alcohol and Water of the following Specific Gravities (Drinkwater) :—

Specific Gravity at 60° F.	Alcohol by weight in 100 parts.	Specific Gravity at 60° F.	Alcohol by weight in 100 parts.	Specific Gravity at 60° F.	Alcohol by weight in 100 parts.	Specific Gravity at 60° F.	Alcohol by weight in 100 parts.	Specific Gravity at 60° F.	Alcohol by weight in 100 parts.
1·0000	0·00	0·9967	1·78	·9934	3·67	·9901	5·70	·9869	7·85
·9999	0·05	·9966	1·83	·9933	3·73	·9900	5·77	·9868	7·92
·9998	0·11	·9965	1·89	·9932	3·78	·9899	5·83	·9867	7·99
·9997	0·16	·9964	1·94	·9931	3·84	·9898	5·89	·9866	8·06
·9996	0·21	·9963	1·99	·9930	3·90	·9897	5.96	·9865	8·13
·9995	0·26	·9962	2·05	·9929	3·96	·9896	6·02	·9864	8·20
·9994	0·32	·9961	2·11	·9928	4.02	·9895	6·09	·9863	8·27
·9993	0·37	·9960	2·17	·9927	4·08	·9894	6·15	·9862	8·34
·9992	0·42	·9959	2·22	·9926	4·14	·9893	6·22	·9861	8·41
·9991	0·47	·9958	2·28	·9925	4·20	·9892	6·29	·9860	8·48
·9990	0·53	·9957	2·34	·9924	4·27	·9891	6·35	·9859	8·55
·9989	0.58	·9956	2·39	·9923	4·33	·9890	6·42	·9858	8·62
·9988	0·64	·9955	2·45	·9922	4·39	·9889	6·49	·9857	8·70
·9987	0·69	·9954	2·51	·9921	4·45	·9888	6·55	·9856	8·77
·9986	0·74	·9953	2·57	·9920	4·51	·9887	6·62	·9855	8·84
·9985	0·80	·9952	2·62	·9919	4·57	·9886	6·69	·9854	8·91
·9984	0·85	·9951	2·68	·9918	4·64	·9885	6·75	·9853	8·98
·9983	0·91	·9950	2·74	·9917	4·70	·9884	6·82	·9852	9·05
·9982	0·96	·9949	2·79	·9916	4·76	·9883	6·89	·9851	9·12
·9981	1·02	·9948	2·85	·9915	4·82	·9882	6.95	·9850	9·20
·9980	1·07	·9947	2·91	·9914	4·88	·9881	7·02	·9849	9·27
·9979	1·12	·9946	2·97	·9913	4·94	·9880	7·09	·9848	9·34
·9978	1·18	·9945	3·02	·9912	5·01	·9879	7·16	·9847	9·41
·9977	1·23	·9944	3·08	·9911	5·07	·9878	7·23	·9846	9·49
·9976	1·29	·9943	3·14	·9910	5·13	·9877	7·30	·9845	9·56
·9975	1·34	·9942	3·20	·9909	5·20	·9876	7·37	·9844	9·63
·9974	1·40	·9941	3·26	·9908	5·26	·9875	7·43	·9843	9·70
·9973	1·45	·9940	3·32	·9907	5·32	·9874	7·50	·9842	9·78
·9972	1·51	·9939	3·37	·9906	5·39	·9873	7·57	·9841	9·85
·9971	1·56	·9938	3·43	·9905	5·45	·9872	7·64	·9840	9·92
·9970	1·61	·9937	3·49	·9904	5·51	·9871	7·71	·9839	9·99
·9969	1·67	·9936	3·55	·9903	5·58	·9870	7·78	·9838	10·07
·9968	1·73	·9935	3·61	·9902	5·64				

This table is founded on synthetic experiments, in which eleven different mixtures of alcohol and water were made, containing respectively 0·5, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 per cent. of alcohol by weight: the alcohol employed had a specific gravity of 0·7938 at 60°.

Proportion of Absolute Alcohol by Weight in 100 *parts of Spirit, of different Specific Gravities at* 60 F.
(Fownes. *Phil. Trans.* 1847.)

Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.
0	1.0000	25	·9652	51	·9160	76	·8581
0·5	·9991	26	·9638	52	·9135	77	·8557
1	·9981	27	·9623	53	·9113	78	·8533
2	·9965	28	·9609	54	·9090	79	·8508
3	·9947	29	·9593	55	·9069	80	·8483
4	·9930	30	·9578	56	·9047	81	·8459
5	·9914	31	·9560	57	·9025	82	·8434
6	·9898	32	·9544	58	·9001	83	·8408
7	·9884	33	·9528	59	·8979	84	·8382
8	·9869	34	·9511	60	·8956	85	·8357
9	·9855	35	·9490	61	·8932	86	·8331
10	·9841	36	·9470	62	·8908	87	·8305
11	·9828	37	·9452	63	·8886	88	·8279
12	·9815	38	·9434	64	·8863	89	·8254
13	·9802	39	·9416	65	·8840	90	·8228
14	·9789	40	·9396	66	·8816	91	·8199
15	·9778	41	·9376	67	·8793	92	·8172
16	·9766	42	·9356	68	·8769	93	·8145
17	·9753	43	·9335	69	·8745	94	·8118
18	·9741	44	·9314	70	·8721	95	·8089
19	·9728	45	·9292	71	·8696	96	·8061
20	·9716	46	·9270	72	·8672	97	·8031
21	·9704	47	·9249	73	·8649	98	·8001
22	·9691	48	·9228	74	·8625	99	·7969
23	·9678	49	·9206	75	·8603	100	·7938
24	·9665	50	·9184				

In this table every alternate number is the result of a direct synthetical experiment; absolute alcohol and distilled water being weighed out in the proper proportions, and mixed by agitation in stoppered bottles; after a lapse of three or four days, each specimen was brought exactly to 60° F. and the specific gravity determined with great care.

	TYPE, AMMONIA. $= \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N.$	TYPE, HYDROGEN. $= \left.\begin{matrix}H\\H\end{matrix}\right\}$
IDES.	NITRIDES. (Phosphides.)	METALS. (Both simple and compound.)
ases.	**Nitrides of bases.**	**Metals of bases.**
metallic cyanides, 'potassium (KCy); f potassium.	1. *Primary nitrides, e.g.* amide of potassium, $\left.\begin{matrix}K\\H\\H\end{matrix}\right\}N.$	1. *Primary metals*, or *hydrides of metals, e.g.* hydride of copper, Cu_2H.
. . . .	2. *Secondary nitrides* (unknown as yet).	2. *Secondary metals*, or *metals properly so called, e.g.* potassium, $\left.\begin{matrix}K\\K\end{matrix}\right\}$; stibiotriethyl, $\left.\begin{matrix}Sb'''\\(C_4H_5)_3\end{matrix}\right\}$.
. . . .	3. *Tertiary nitrides, e.g.* nitride of potassium, $\left.\begin{matrix}K\\K\\K\end{matrix}\right\}N.$	. . . .
lcohols.	**Nitrides of alcohols,** or bases from alcohols.	**Metals of alcohols.**
des, or *hydrocyanic riles, e.g.* acetoni- y).	1. *Primary nitrides, e.g.* ethylia, $\left.\begin{matrix}C_4H_5\\H\\H\end{matrix}\right\}N.$	1. *Primary metals*, or *hydrides of the alcohols, e.g.* marsh gas, $\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}$; benzole, $\left.\begin{matrix}C_{12}H_5\\H\end{matrix}\right\}$.
. . . .	2. *Secondary nitrides, e.g.* diethylia, $\left.\begin{matrix}C_4H_5\\C_4H_5\\H\end{matrix}\right\}N.$	2. *Secondary metals*, or *alcohol radicles, e.g.* ethyl, $\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}$; amyl, $\left.\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right\}$.
. . . .	3. *Tertiary nitrides, e.g.* triethylia, $\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N.$	. . . .
aldehyds.	**Nitrides of aldehyds.**	**Metals of aldehyds.**
nides (not known	1. *Primary nitrides.*	1. *Primary metals*, or *hydrides of aldehyds, e.g.* olefiant gas, $\left.\begin{matrix}C_4H_3\\H\end{matrix}\right\}$.
. . . .	2. *Secondary nitrides.*	2. *Secondary metals* (not yet obtained).
. . . .	3. *Tertiary nitrides.* (All these classes are as yet unknown.)	. . . .
acids.	**Nitrides of acids.**	**Metals of acids.**
nides, e.g. cyanide $C_{14}H_5O_2$, Cy); free , Cy).	1. *Primary nitrides, e.g.* benzamide, $\left.\begin{matrix}C_{14}H_5O_2\\H\\H\end{matrix}\right\}N$; succinamide, $\left.\begin{matrix}(C_8H_4O_4)''\\H_2\\H_2\end{matrix}\right\}N_2$.	1. *Primary metals*, or *hydro-acids, e.g.* hydride of benzoyl, $\left.\begin{matrix}C_{14}H_5O_2\\H\end{matrix}\right\}$; hydrochloric acid, $\left.\begin{matrix}Cl\\H\end{matrix}\right\}$; hydrocyanic acid, $\left.\begin{matrix}Cy\\H\end{matrix}\right\}$.
. . . .	2. *Secondary nitrides, e.g.* succinimide, $\left.\begin{matrix}(C_8H_4O_4)''\\(C_8H_4O_4)''\\H_2\end{matrix}\right\}N_2$; hippuric acid, $\left.\begin{matrix}C_4H_2O_4\\C_{14}H_5O_2\\H\end{matrix}\right\}N.$	2. *Secondary metals*, or *radicles, e.g.* benzoyl, $\left.\begin{matrix}C_{14}H_5O_2\\C_{14}H_5O_2\end{matrix}\right\}$; chlorine, $\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}$; cyanogen, $\left.\begin{matrix}Cy\\Cy\end{matrix}\right\}$.
. . . .	3. *Tertiary nitrides, e.g.* dibenzoyl salicylamide, $\left.\begin{matrix}C_{14}H_5O_2\\C_{14}H_5O_2\\C_{14}H_5O_4\end{matrix}\right\}N$; free nitrogen, N''', N.	. . . .
. . . .	**Salts of amides,** *e.g.* hydrargobenzamide, $\left.\begin{matrix}C_{14}H_5O_2\\Hg\\H\end{matrix}\right\}N.$	In this division many of those already referred to other classes would find their places, such for instance as the cyanides of the alcohols, which contain the electro-negative radicle (cyanogen) of cyanic acid, and the electro-positive radicle of the alcohol.
. . . .	**Alkalamides,** or amides derived from alkaloids or organic bases instead of from ammonia, *e.g.* oxanilide, $\left.\begin{matrix}(C_4O_4)''\\(C_{12}H_5)_2\\H_2\end{matrix}\right\}N_2$; ethyl-acetamide, $\left.\begin{matrix}C_4H_3O_2\\C_4H_5\\H\end{matrix}\right\}N.$	
. . . .	. . . .	

Table of the Tension of Aqueous Vapour expressed in Inches of Mercury, at 32° F., for each degree F. between 0° and 100°.

Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.
0	0·0439	26	0·1395	51	0·3742	76	0·8964
1	0·0459	27	0·1457	52	0·3882	77	0·9266
2	0·0481	28	0·1522	53	0·4026	78	0·9577
3	0·0503	29	0·1589	54	0·4175	79	0·9898
4	0·0526	30	0·1660	55	0·4329	80	1·0227
5	0·0551	31	0·1733	56	0·4488	81	1·0566
6	0·0576	32	0·1810	57	0·4653	82	1·0915
7	0·0603	33	0·1883	58	0·4822	83	1·1274
8	0·0630	34	0·1959	59	0·4997	84	1·1643
9	0·0659	35	0·2038	60	0·5178	85	1·2023
10	0·0689	36	0·2119	61	0·5364	86	1·2413
11	0·0721	37	0·2204	62	0·5556	87	1·2815
12	0·0753	38	0·2291	63	0·5755	88	1·3228
13	0·0788	39	0·2381	64	0·5959	89	1·3652
14	0·0823	40	0·2475	65	0·6170	90	1·4088
15	0·0861	41	0·2571	66	0·6388	91	1·4537
16	0·0899	42	0·2672	67	0·6612	92	1·4998
17	0·0940	43	0·2775	68	0·6843	93	1·5471
18	0·0982	44	0·2882	69	0·7081	94	1·5958
19	0·1027	45	0·2993	70	0·7327	95	1·6457
20	0·1073	46	0·3108	71	0·7580	96	1·6971
21	0·1121	47	0·3226	72	0·7841	97	1·7498
22	0·1171	48	0·3349	73	0·8109	98	1·8039
23	0·1223	49	0·3476	74	0·8386	99	1·8595
24	0·1278	50	0·3607	75	0·8671	100	1·9170
25	0·1335						

This table is computed from Regnault's experiments, and is taken from Dixon's "Treatise on Heat" (p. 257).

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THE END.

ADDITIONAL CORRECTIONS IN PART I.

Page 166, 4 lines from top, for 316, read 416.
,, 233, 9 ,, ,, ,, 0·044, ,, 0·00146.
,, ,, 10 ,, ,, ,, 0·18 ,, 0·00603.
,, 242, 2 ,, bottom of table, for 4·67, read 4·76.
,, ,, 4 ,, ,, ,, ,, 8·10, ,, 8·14.
,, ,, 12 ,, ,, ,, ,, 40·19, ,, 42·19.
,, 400, 7 ,, bottom, ,, M ,, *it.*
,, 407, 12 and 22 lines from top, for *electromagnetic*, read *magneto electric*.

ADDITIONAL CORRECTIONS IN PART II.

Page 652, 8 lines from top, at beginning of line, for 1, read 3.
,, 726, 2 ,, bottom, ,, KO, SO_4, read KO, SO_3.
,, 772, 9 ,, ,, after *distillation*, insert *of oxalate*.
,, 779, 3 ,, top, for 2 [at beginning of line], read 3.
,, 780, 11 ,, ,, ,, *are*, read *afford*.
,, ,, 13 ,, bottom, substitute the following equation for the one given :—

$$6\,(CuCl,\ 3\,H_3N) = 3\,Cu_2Cl + 3\,H_4NCl + 14\,H_3N + N.$$

,, 851, 14 ,, bottom, for 56·74, read 55·74.
,, 852, 7 ,, top, ,, 64·7, ,, 63·7.
,, ,, 15 ,, ,, ,, 72·7, ,, 71·7.
,, 956, last line, after *distilling*, dele 8 *parts of*.
,, 1054, 11 lines from top, for 16, read 32.
,, 1066, 9 ,, bottom, ,, *diplatosamine*, read *diplatinamine*.
,, 1067, 7 ,, ,, ,, PtH_3NCl, ,, PtH_3NCl_2.

CORRECTIONS IN PART III.

Page 4, 11 lines from top, for *substituted for a portion of the hydrogen of*, read *introduced into*.
,, 29, 9 ,, bottom, ,, (C_4H_3, C_2H_3), read (C_8H_3, C_2H_3).
,, 41, 6 ,, top, ,, $C_{16}H_5NO_6$, ,, $C_{16}H_5NO_4$
,, 45, 20 ,, bottom, ,, $C_4H_{11}N$, ,, $C_8H_{11}N$.
,, 50, 9 ,, top ,, *takes place*, ,, *is formed*.
,, 59, 8 ,, bottom, ,, $(3\,HO, C_{12}H_5O_5)$, read $(3\,HO, C_{24}H_{13}O_{15})$.
,, 69, 10 ,, ,, before *citraconic* insert *anhydrous*.
,, 71, 3 ,, ,, for $C_{14}H_{19}O_{19}$, 5 HO, read $C_{24}H_{19}O_{19}$, 5 HO.
,, 72, 9 ,, ,, ,, *tartrate of potash*, ,, *tartrate of copper*.
,, 139, 2 ,, ,, ,, *groups of acids*, ,, *group of acids to which it belongs*.
,, 143, 19 ,, ,, ,, $(CaO, HO, C_4H_5O, S_2O_6, 2\,Aq)$, read $(CaO, C_4H_5O, S_2O_6, 2\,Aq)$.
,, 162, 16 ,, ,, dele 214.
,, ,, 15 ,, ,, for 0·965, read 0·975.
,, ,, 12 ,, ,, ,, 608, ,, 662.
,, ,, 4 ,, ,, ,, 1·0229, ,, 1·0929.
,, 170, 7 ,, top, ,, *silicic ether*, read *disilicate of ethyl*.
,, 172, 20 ,, bottom, ,, 1·0229 ,, 1·0929.
,, 173, 5 ,, top, formula for alcohol, $2\,(C_4HO, H_5O)$, read $2\,(C_4H_5O, HO)$.
,, ,, 20 ,, bottom, for 0·965, read
,, 175, 11 ,, ,, ,, $2\,C_4H_5O$, C [redacted]

Page 175, 8 lines from bottom, for $2\,C_4H_5O, C_2NO$, read $2\,(C_4H_5O, C_2NO)$.
,, ,, 5 ,, ,, ,, $2\,C_{10}H_{11}O, C_2NO$, ,, $2\,(C_{10}H_{11}O, C_2NO)$.
,, 180, 21 ,, ,, ,, $4\,HO$, ,, $6\,HO$.
,, 181, 9 ,, ,, ,, $C_4H_3Cl_2O$, ,, $C_4H_2Cl_3O$.
,, 182, 6 ,, ,, ,, $3\,HO$, ,, $2\,HO$.
,, ,, last line ,, KCl, ,, HCl.
,, 184, 11 lines from bottom, ,, C_4Cl, HO_2 ,, $C_4Cl_3HO_3$.
,, 185, 18 ,, top, ,, (at end of line) 2 Cl, read 2 CO.
,, ,, 24 ,, ,, ,, 3 HO, read 2 HO.
,, 187, 11 ,, bottom, ,, *homologue*, read *analogue*.
,, 190, 17 ,, ,, ,, *ethyl* ,, *decyl*.
,, 191, 6 ,, top, ,, *iodide of zinc*, read *iodide of amyl*.
,, 203, 3 ,, ,, ,, $C_{30}H_{17}N$, ,, $C_{30}H_{21}N$.
,, 212, 19 ,, ,, ,, $C_{16}C_{17}H_2N$, ,, $C_{16}H_{17}, H_2N$.
,, 213, 4 ,, ,, ,, *alcohol*, ,, *sodium-alcohol*.
,, 216, 24 ,, bottom, ,, *electropositive*, ,, *electronegative*.
,, 218, 6 ,, top, ,, (C_4H_5, ZnO), ,, (C_4H_5O, ZnO).
,, 224, 19 ,, bottom, ,, $4\,(C_4H_6As)O$, ,, $4\,(C_4H_6)AsO$.
,, ,, 6 ,, ,, omit I in the formula.
,, 262, 16 ,, ,, for $2\,(C_{15}H_6O_6)$,, $2\,(C_{15}H_6NO_6)$.
,, 266, 11 ,, top, after $(C_{16}H_{14})$ insert N.
,, 290, 3 ,, ,, for $C_{64}H_{38}N_2O_{18}$, read $C_{64}H_{38}N_2O_{16}$.
,, 304, 2 ,, ,, instead of the formula for acetonic acid, read [$2\,HO, C_{16}H_{14}O_{10} = 2\,(HO, C_2HO_3), 2\,C_6H_6O_2$].
,, 322, 15 ,, ,, ,, $2\,HO, C_{24}H_{22}O_{20}$, read $2\,HO, C_{24}H_{20}O_{22}$.
,, 324, first line, ,, $CuO, C_{12}H_{10}O_{10}, 4\,Aq$, read $2\,CuO, C_{12}H_{10}O_{10}, 4\,Aq$.
,, 334, 19 ,, top, ,, *tartralic*, read *tartrelic*.
,, ,, 20 ,, ,, ,, *tartrelic*, ,, *tartralic*.
,, 335, 21 ,, ,, first word, for *maleic*, read *malic*.
,, 345, 8 ,, bottom, and p. 349, 7 lines from top, for $C_{28}H_{16}O_{16}$, read $C_{28}H_{16}O_{20}$.
,, 350, 3 ,, top, the bracket is misplaced; the formula should be [$2(KO, 2\,HO, C_{14}H_2O_7) + 3\,HO, C_{14}H_2O_7, 2\,Aq$].
,, 352, 10 ,, top, dele *isomeric with ellagic acid ; it is*.
,, 387. The formulæ of all the acids in the third column of the table, except the oxalic, should contain H_2 more than is given.
,, 414, 9 lines from top, for *this formic*, read *thioformic*.
,, 453, 13 ,, bottom, for BzH, 2 (HO, BzO), read 2 BzH, (HO, BzO).
,, 454, 10 ,, top, ,, $C_{14}H_9, H_2N$, ,, $C_{14}H_7, H_2N$.
,, 463, 9 ,, bottom, ,, $HO, C_{14}H_4(H_2N)_2O_3$,, $HO, C_{14}H_4(H_2N)O_3$.
,, 467, 10 ,, top, ,, $C_{14}H_7N$, ,, $C_{14}H_5N$.
,, 481. The formula for gaultherate of methyl in the table is transposed ; it should be $C_2H_3O, C_{14}H_4(C_2H_3)O_5$.
,, 485, 22 lines from bottom, $HO, C_{14}H_8NO_7$, read $HO, C_{18}H_8NO_7$.
,, 527, 20 ,, top, for HO, InO_3, ,, HO, In, H, O_3.
,, 538, 18 ,, bottom, ,, $HO, C_{28}H_{22}O_{19}$, read $HO, C_{28}H_{13}O_{18}$.
,, 572, 5 ,, ,, ,, *lime*, read *iron*.
,, 595. In table, the line of formulæ for ferridcyanide of potassium and barium should be $KBa_2C_{12}N_6Fe_2$; $6\,HO, KBa_2$, Fdcy, 6 Aq.
,, 645, 22 lines from top, dele *the*.
,, 752, 4 ,, bottom, for *about*, read *more than*.
,, 761, top of table opposite hydrocyanic acid, for 14 read 13·5.
,, 762, opposite bisulphide of carbon, ,, 40 ,, 38.
,, ,, ,, fluoride of boron, ,, 34·9 ,, 39·4.
,, ,, ,, sesquichlor. carbon, liquid, ,, $\frac{C_2Cl_3}{2}$,, $\frac{C_2Cl_3}{4}$

of small air-gauges, which he enclosed in the tubes employed for the condensation (fig. 120). These gauges consisted of a somewhat conical capillary tube of glass, which was divided into parts of equal capacity, by introducing into the tube a globule of mercury, shown at *a*, which was made to occupy each part of the tube in succession; the length of the little cylinder into which the mercury was reduced in each portion of the tube was marked upon the glass with black varnish. The mercury was then transferred towards the widest extremity, and the tube was sealed at its narrow end. A known volume of air was thus included, and by the compression which this air experienced in the course of the experiment (the bulk being inversely as the pressure) the elastic force of the gas under examination was easily calculated. It is remarkable that many of these condensed liquids expand upon the application of heat more rapidly than the gases themselves. It has been also found that Marriotte's law (26), according to which the elasticity of a gas increases directly as the pressure, although correct for pressures at some distance above the point of condensation, does not hold good as this term is approached; probably, as suggested by Berzelius, because the distance to which the particles are separated is not sufficient entirely to overcome the cohesive force, which increases in power the more nearly the point of condensation is reached (see *note*, page 36, and page 170).

Although indications of this departure from Marriotte's law have been observed at common temperatures, with some of the more condensible gases, such as sulphurous acid, sulphuretted hydrogen, cyanogen, and ammonia, it was most distinctly exhibited in the experiments of Cagniard de Latour (*Ann. de Chimie*, II. xxi. and xxii). De Latour partially filled some strong glass tubes with water, with alcohol, with ether, and with some other liquids, furnished them with gauges, and hermetically sealed them. He then cautiously raised the temperature. The alcohol (sp. gr. 0·844), which occupied ⅖ the capacity of the tube, gradually expanded to double its volume, and then suddenly disappeared in vapour, at a temperature of 497¾° F.; it then exerted a pressure of about 119 atmospheres. Ether becomes gaseous at 392°, in a space equal to double its original bulk, exerting a pressure of 37½ atmospheres; whereas, if Marriotte's law held good in these cases, calculating from the volume of vapour which a certain bulk of each liquid yields under the atmospheric pressure, ether should have exerted a force equal to about 157 atmospheres, and alcohol of at least 318. Water was found to become gaseous in a space equal to about four times its original bulk, at a temperature of about 773°

(that of melting zinc). So great was the solvent power of water on glass, at this high temperature, that the addition of a little carbonate of soda was necessary to diminish the action on the glass, which frequently gave way until this expedient was adopted. As the vapours cooled, a point was observed at which a sort of cloud filled the tube, and, in a few moments after, the liquid suddenly reappeared.

It will be seen from the subjoined table, that even after the liquid has wholly disappeared, the increase in the elastic force of the vapour, as the temperature rises, is as rapid as before it had all volatilized, and indeed it continues to increase in a proportion far greater than that which would be produced in air by an equal elevation of temperature. Atmospheric air, under a pressure of 37·5 atmospheres at 370°F., would, at 482°, exert a force of 42·4, and at 617° of 48·6 atmospheres, whereas the corresponding pressures with ether were 86·3 and 130·9 atmospheres. In the case of the two experiments with ether, the increase in elasticity is greatest at first in the tube which contains the smallest proportion of liquid; probably because the influence of cohesive attraction is more completely overcome in the tube which admits of the greatest distance between the particles of the vapour:—

Cagniard de Latour's Experiments.

Temperature. °F.	Ether.		Bisulphide of carbon.
	Volume, as liquid 7 parts, as vapour 20 parts.	Volume, as liquid 3½ parts, as vapour 20 parts.	Volume, as liquid 8 parts, as vapour 20 parts.
	Pressure in atmospheres.	Pressure in atmospheres.	Pressure in atmospheres.
212	5·6		4·2
234·5	7·9		5·5
257	10·6	14·0	7·9
279·5	12·9	17·5	10·0
302	18·0	22·5	13·0
324·5	22·2	28·5	16·5
347	28·3	35·0	20·2
369·5	37·5*	42·0*	24·2
392	48·5	50·5	28·8
414·5	59·7	58·0	33·6
437	68·8	63·5	40·2
459·5	78·0	66·0	47·5
482	86·3	70·5	57·2
504·5	92·3	74	66·5*
527	104·1	78	77·8
549·5	112·7	81	89·2
572	119·4	85	98·9
594·5	123·7	89	114·3
617	130·9	94	129·6
628·2			135·5

* At this point the liquid had entirely disappeared as vapour.

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